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Inorganic
Quantitative Analysis

Inorganic Quantitative Analysis

By

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Professor of Chemistry in Vassar College

Philadelphia . THE BLAKISTON COMPANY . Toronto

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PRINTED IN THE UNITED STATES OF AMERICA
BY THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

It is always important to get off to a good start in any undertaking. Particularly in a first course of study in quantitative chemistry is it desirable that the initial experimental work be of a nature that will stress the necessity of rigor without overwhelming the student with a deluge of minutiae. As a beginning I prefer the determination of the sensitivity of the balance. Among the advantages are these: here the paramount importance of precision is emphasized immediately; the contribution of a large number of simple and relevant factors to a single, final result is demonstrated; and the fidelity of a delicate mechanism is manifested. Furthermore, here one gets the feel of the balance; as a result, in subsequent experiments there is a command of confidence in the ability to deliver accurate results. If this is followed by the calibration of a volumetric instrument where weighings to the nearest milligram will satisfy, then sufficient familiarity with the balance is attained to meet the more fastidious demands of weighing to a constant weight in later work. For such reasons Chapter 2 on general operations and equipment is followed by a discussion of accuracy, precision, errors and significant figures, and then by the use of the balance and instructions in volumetric calibrations. Volumetric principles and determinations precede those for gravimetric work, though for courses in which the custom is to reverse this order the first four chapters may be followed by Chapters 13, 14 and 15. In each subdivision of the subject the experimental part immediately follows the chapter or chapters dealing with the theoretical principles.

The theory and experimental work included in this volume should require a year's time. By choosing typical procedures from the sections dealing with volumetric and gravimetric analysis and omitting the more specialized experiments of the last several chapters, the material for a one-semester course may be selected. In Chapter 7 a treatment more extensive than customary is given for calculating the data for titration curves. Lack of time in one-semester courses may necessitate omission of the material printed in extract type. However, when time allows, a study of conditions, unusual as compared with more remote points, prevailing in the majority of titrations at the beginning of the neutralization and immediately around the stoichiometric point is worth the added attention. Though not greatly altering the course of the curves, these detailed calculations furnish an excellent illustration of the obligation of thorough-

ness, and also provide further opportunity for the observation of common ion and hydrolytic effects.

It seems to me that a course in elementary quantitative analysis should not presume a previous knowledge of chemistry other than that acquired in a sound course in general chemistry and qualitative analysis. In preparing the text I have kept this in mind. Occasionally, as in presenting the theory of indicators or in taking up the efficiency of desiccants, I find it desirable to include concepts which the student will explore more fully in later studies; however, in such cases the presentation has been kept on a simple basis. On the other hand, it hardly seems necessary to review such foundation laws as that of combining weights or the law of mass action, which have already been studied and applied.

During the past decade and more I have used for my own classes in quantitative chemistry the excellent texts of Blasdale; Booth and Damerell; Fales and Kenny; Kanning; Kolthoff and Sandell; Pierce and Haenisch; Rieman, Neuss and Naiman; Talbot (Hamilton and Simpson); and Willard and Furman. My own thinking has been influenced in large measure by the pedagogy of these authors and my indebtedness to them is unqualified. I am grateful to Dr. Mary O. Hillis for contributing many hours to methods of presenting various topics and for her valuable criticism of many sections of the manuscript. My thanks are also due to Mrs. Charles M. Kuhbach who not only took great pains in typing the manuscript but also made many helpful editorial suggestions. The advice of The Blakiston Company was frequently sought and generously given; particular acknowledgment is due to the Editor, Dr. James B. Lackey, for his interest and attention. I shall heartily welcome any notice of errors and of ideas for improvement of the text.

CARROLL W. GRIFFIN

Poughkeepsie, New York
March 1949

CONTENTS

PREFACE v

1. INTRODUCTION 1
2. GENERAL OPERATIONS AND EQUIPMENT 4
3. ACCURACY, PRECISION, ERRORS AND SIGNIFICANT FIGURES . . 23
4. THE ANALYTICAL BALANCE. WEIGHING 39
5. CALIBRATION OF VOLUMETRIC APPARATUS 65
6. VOLUMETRIC ANALYSIS. FUNDAMENTAL PRINCIPLES 74
7. NEUTRALIZATION 86
8. ACIDIMETRY AND ALKALIMETRY 130
9. OXIDATION AND REDUCTION I. STOICHIOMETRIC RELATIONS AND CALCULATIONS 152
10. OXIDATION AND REDUCTION II. THEORY 164
11. OXIDATION AND REDUCTION III. EXPERIMENTAL 187
    - Potassium Permanganate Processes 187
    - Ceric Processes 199
    - Potassium Dichromate Processes 201
12. OXIDATION AND REDUCTION IV. IODINE PROCESSES 204
13. GRAVIMETRIC ANALYSIS. FUNDAMENTAL PRINCIPLES 221
14. COPRECIPITATION 238
15. GRAVIMETRIC ANALYSIS. EXPERIMENTAL 248
16. VOLUMETRIC ANALYSIS BY PRECIPITATION METHODS 281
17. POTENTIOMETRIC TITRATIONS 293
18. ELECTROANALYSIS 303
19. COLORIMETRY 317

APPENDIX 325
- Care of Platinum Ware 327
- References 329
- Tables 331
  - Logarithms 338

INDEX 357

LABORATORY EXPERIMENTS

Determination of the Sensitivity of the Balance 50
Weighing 51
Calibration of a Set of Weights 57
Calibration of a Volumetric Flask 66
Calibration of a Pipet 70
Calibration of a Buret 71

Acidimetry—Alkalinity

Preparation of 0.1 *N* Hydrochloric Acid Solution 130
Preparation of 0.1 *N* Sodium Hydroxide Solution 131
Determination of the Relative Concentrations of Acid and Base Solutions 132
Standardization of Hydrochloric Acid Solution 132
Preparation of Sodium Carbonate Standard 133
Preparation of Standard Hydrochloric Acid Solution from Constant-Boiling Acid 135
Standardization of Sodium Hydroxide Solution:
(a) With Potassium Biphthalate 136
(b) With Sulfamic Acid 136
(c) With Benzoic Acid 137
Determination of the Acidity of Vinegar 138
Determination of the Acidity of Oxalic Acid 138
Determination of the Acidity of Boric Acid 139
Determination of the Alkalinity of Soda Ash 140
Determination of Carbonate and Hydroxide in a Single Sample 141
Determination of Nitrogen in an Organic Substance 143
Determination of Nitrogen in an Inorganic Substance 148

Oxidation-reduction

permanganate processes

Preparation of 0.1 *N* Potassium Permanganate Solution . . . 188
Standardization of Potassium Permanganate Solution:
(a) With Sodium Oxalate 189
(b) With Arsenious Oxide 189
(c) With Iron Wire 190

Determination of Iron in an Ore 190
Zimmermann-Reinhardt Reduction 191
Jones Reductor 192
Silver Reductor 194
Analysis of Pyrolusite 195
Determination of Calcium 196
Determination of Hydrogen Peroxide 198

CERIC PROCESSES

Preparation of 0.1 *N* Ceric Ammonium Sulfate Solution . . . 200
Standardization of Ceric Ammonium Sulfate Solution:
(a) With Arsenious Oxide 200
(b) With Iron Wire 201
Determination of Iron in an Ore 201

POTASSIUM DICHROMATE PROCESSES

Preparation of 0.1 *N* Solution of Potassium Dichromate . . 202
Standardization of Potassium Dichromate Solution . 202
Determination of Iron in an Ore 203

IODINE PROCESSES

Preparation of Starch Indicator Solution 205
Preparation of 0.1 *N* Iodine Solution 206
Standardization of Iodine Solution 206
Determination of Sulfur in Steel 207
Determination of Antimony in Stibnite 208
Determination of Antimony in Tartar Emetic 209
Preparation of 0.1 *N* Sodium Thiosulfate Solution . . . 210
Standardization of Sodium Thiosulfate Solution:
(a) With Potassium Dichromate . . 212
(b) With Potassium Bromate, Iodate or Bi-iodate . 213
(c) With Metallic Copper 214
Determination of Copper in an Ore 215
Determination of Available Chlorine in Bleaching Powder . 216
Determination of Hydrogen Peroxide 217

GRAVIMETRIC ANALYSIS

Determination of Chlorine in a Soluble Chloride 248
Determination of Sulfur in a Soluble Sulfate 251
Determination of Sulfur in a Sulfide Ore 254
Determination of Sulfur in Coal. Eschka Method . 255
Determination of Phosphorus in Phosphate Rock:
(a) Phosphomolybdate Method 256
(b) Short Method 259
Determination of Iron 260

ANALYSIS OF LIMESTONE
(a) Moisture and Loss on Ignition 263
(b) Silica 264
(c) Combined Oxides 266
(d) Calcium 267
(e) Magnesium 269
(f) Carbon dioxide 270
DETERMINATION OF LEAD 274
DETERMINATION OF NICKEL. DIMETHYLGLYOXIME METHOD . 276
DETERMINATION OF ALUMINUM. OXINE METHOD . . . 277

VOLUMETRIC PRECIPITATION METHODS

DETERMINATION OF CHLORIDE. MOHR METHOD . . 283
PREPARATION AND STANDARDIZATION OF SILVER NITRATE SOLUTION. 283
DETERMINATION OF CYANIDE. LIEBIG METHOD 285
DETERMINATION OF CHLORIDE. VOLHARD METHOD. . 287
DETERMINATION OF CHLORIDE. FAJANS METHOD. 290

POTENTIOMETRIC TITRATIONS

ACID-BASE TITRATION USING THE HYDROGEN ELECTRODE. . . 300
ACID-BASE TITRATION USING THE QUINHYDRONE OR THE GLASS ELECTRODE 301
POTENTIOMETRIC TITRATION OF IRON. 301
PRECIPITATION-POTENTIOMETRIC TITRATION: DETERMINATION OF CHLORIDE. 302

ELECTROANALYSIS

DETERMINATION OF COPPER. 308
DETERMINATION OF COPPER AND NICKEL IN AN ALLOY 311
ANALYSIS OF BRASS
(a) Tin 312
(b) Lead 313
(c) Copper 314
(d) Iron 314
(e) Zinc 314

COLORIMETRY

DETERMINATION OF MANGANESE IN STEEL 322

FOREWORD TO THE STUDENT

THE ULTIMATE goal of every scientific journey has the peculiarity, which at the same time is its fascination, of belonging to the sphere of the unknown. At the furthest borders of encompassed knowledge, of that area which has been probed and charted by the patient and often ingenious labors of man, one stands at the pinnacle of recorded human achievement—only to see beyond far vaster regions still wrapped in obscurity and mystery. It is this realm of the unknown with its promise of discovery, its invitation to behold that which never before has been revealed to man, that marks the aim of scientific enterprise, as goal, as challenge and as final reward for the dedication and the effort required of him who aspires to become a scientist.

There is always a compelling persuasion in discovery. This is as it should be; otherwise the accumulation of knowledge loses something of its zest. Much has been said about the exhilaration of reaching the horizon from which one may look out upon and then explore the unknown. But how little has been told us of the joys of the journey to these borders. Though already well charted, the route is no parkway for effortless travel. We look about and see such a threatening expanse over which we must pass before we emerge upon higher ground that sometimes we are all but dismayed. Just how do we get there? Not by a superficial survey, by random wandering, nor by unorganized thrashing at the underbrush; one cuts through to the broad avenues which lead to the boundless stretch beyond by an orderly orientation, through a firm resolution to take each barricade one by one, and in a constant vigilance for the unforeseen. The rewards of this preliminary ascent which we are about to begin are rich and the labor involved brings its own satisfaction. For while we are yet striving toward the goal we know the joy of progress and the gratification which comes with a growing power of perception.

Once the terrain of higher ground has been reached we shall find many avenues leading on to the horizon. When these have been gained the journey will be more swift. It makes little difference which of these highways later we may choose; the habits of perseverance, exactness, orderliness and impartiality of judgment, which we learn as we clear these simpler approaching pathways, will be found to be the means also of surmounting obstacles as yet remote. And nowhere more than in quantitative analysis does one acquire discipline in avoiding detours; nowhere

does one learn better the priceless value of assurance gained after each advance through what, a few miles back, might have appeared as a formidable tract; nowhere else does one more quickly sense with what sure success careful thought and skilful technique sweep away entanglements.

Here then is the opportunity for joy: the joy of finding the tasks which lie ahead worthy of the effort, the joy of constructing a pathway cleanly penetrating what was once strange land, and the joy of commanding new knowledge and new skills. Here, at last, we shall find the satisfaction that, having crossed this barrier, we are better seasoned for the further travels. And as each such barrier is met and crossed the disclosure becomes ever clearer that the ultimate goal beyond is no mirage, but is reality itself, worthy of all the labor—and all the joy.

CARROLL W. GRIFFIN

Chapter 1

INTRODUCTION

QUANTITATIVE analysis, as the term implies, is concerned with the determination of the amount of one or more of the constituents present in a substance. If little or nothing is known about the composition of the substance under study it will be necessary to make a qualitative analysis in order to learn what constituents make up the material. The quantitative analysis may be of a gravimetric nature. This involves the separation and weighing of the constituent sought, as such or as one of its compounds of definite composition. The separation may be effected sometimes by extraction (p. 13), by electrolytic deposition (Chapter 18), by evolution as a gas (p. 270), but most often by the precipitation of a compound containing the constituent and bearing a known and invariable mathematical relation to it (Chapter 15). The analysis may be of a volumetric nature. This involves the measurement of the volume of a solution of known concentration which is required to react with the sample. The completion of the desired reaction is marked by such means as the color change of indicator dyes (pp. 100, 184 and Chapter 8) or by the sudden change in some such property as an electrode potential (Chapter 17). The analysis may be accomplished by special methods which lie outside the above two classifications; these depend upon the determination of some specific property of the constituent sought which varies in proportion to the quantity present. The amount of alcohol in a solution, for example, may be determined by taking the specific gravity of the measured distillate from a definite volume of an aqueous solution. Again the index of refraction of many binary mixtures (solutions) will reveal the composition. Further, the intensity of color imparted by a colored component to a solution may be made to indicate the quantity present (Chapter 19). Other methods which make use of optical properties are: those depending upon the rotation of a plane of polarized light by a solution of an optically active compound; those in which the absorption or the scattering of light by a suspension is measured; and spectrographic methods in which the intensity of the lines in the emission spectrum is a measure of the quantity of the constituent.

Chemical analysis is important from both a practical and a theoretical point of view. Chemical industry depends upon analysis for guidance in the purchase of raw materials, as a step by step check on the efficiency

of manufacturing processes and for tests of the final products before marketing. In theoretical chemistry any hypothesis must undergo exhaustive experimental proof before it may be regarded as a generalized statement of fact, and in such tests it is almost always necessary to determine the identity and composition of substances resulting from the study. The practice of analysis therefore may be confined on the one hand to that of the specialized commercial chemist, or it may be an adjunct to the investigations of the physical chemist, the organic chemist, the biochemist and the like. In any event, although there is more of the routine in his work and though his tools as a rule are more common than those of the research chemist, the accountability of the analyst is strict; to meet his responsibilities it is imperative not only that he possess a high degree of technical skill but that he shall become familiar with the chemical and physical characteristics and the behavior of a wide variety of substances. As he learns more about the laws under which chemical reactions operate he also grows in self-reliance and resourcefulness. Many of the laws have already been studied in general chemistry and qualitative analysis. Among those which find wide application in quantitative analysis are the theory of ionization and the law of mass action and chemical equilibrium. Based upon these concepts are the principles of the common ion effect, solubility product, hydrolytic and buffer actions and electrode potentials. Since an elementary understanding of these and other laws (combining weights, etc.) has been achieved previously, we shall proceed to apply them in the study of quantitative analysis without repeating in detail their postulates.

Hardly any of the calculations of quantitative chemistry is complicated, being almost wholly confined to arithmetic and algebra, and seldom calling for anything more involved than a quadratic equation. However, there is some divergence of practice regarding the unit of the chemical equivalent. The gram equivalent weight of an element or compound is defined as the weight in grams which reacts with or is displaced by 1.008 g. of hydrogen or its equivalent. The term gram milliequivalent weight is often employed in calculations; it is the gram equivalent weight divided by 1000. The chief reasons why the latter frequently is used is that it bears the same relation to the former that the milliliter bears to the liter, and by using milliequivalents one avoids fractions as a rule. Thus, for example, 0.05845 g. of sodium chloride (eq. wt. = 58.45) represents 0.001 gram equivalent weight of the salt, or 1 gram milliequivalent weight. Here the use of the milliequivalent weight can claim no greater advantage than the use of pennies rather than dollars could claim in pricing a commodity. (If an article costs 0.50 dollar we may say that it is valued at half a dollar or at 50 cents.) It is true that the number of milliliters of a 1 *N* solution is numerically identical with the

gram milliequivalent weights of solute present: 50 ml. of 1 N solution contains 50 gram milliequivalent weights; however, it is equally obvious that 50 ml. of 1 N solution contains $^{5}\%_{1000}$ or 0.05 gram equivalent weight. Furthermore, in dealing with standard solutions the concentration is not often exactly 1.000 N, and the conversion of A ml. of X normal solution to its equivalent of B ml. of 1.000 N solution, as sometimes is done to establish the number of milliequivalent weights, involves just one extra step. Many analysts therefore prefer to work always on the basis of the larger unit, the gram equivalent weight. It is somewhat surprising that there should be any predilection for one system over the other since either is quite simple in application. In the calculations throughout this book both have been used: unless the student already has developed a choice as a habit in the matter it might be well to employ one and then the other until a personal preference is felt.

Chapter 2

GENERAL OPERATIONS AND EQUIPMENT

DURING the first period in the study of quantitative analysis the student is usually assigned to a desk and a balance. In the compartment of the desk the most commonly used pieces of apparatus will be found, many of which have been encountered in previous courses of study, but some of which will be unfamiliar. It may be necessary to construct such apparatus as wash bottles. Everyone should learn as soon as possible the elementary manipulations involved in bending glass and the like, for the facility of using the hands with dexterity is nowhere more important than in the quantitative laboratory. Equally important is the necessity of absolute cleanliness. All apparatus, reagent bottles and the balance must be immaculate. The satisfaction of carrying out an analysis with accurate results, and the confidence which one has in those results, depend not only upon a thorough understanding of the steps taken throughout the analysis and upon the proper interpretation of the measurements made, but also upon the knowledge that no avoidable error has been allowed to mar those results. This means that every step must be taken with proper attention given to clean apparatus, pure reagents and careful technique. Usually the operations are most quickly and effectively accomplished by proved methods. Some of these will be mentioned in this chapter. There are scores of places in every analysis where errors may creep in; there is only one right way to carry out a piece of work—namely, to see that every step taken is as free from fault as possible.

Even this is not enough. The best of work is of no permanent value unless the right kind of record is made. Entries in a bound notebook should be made in ink, and they should follow a concise, orderly outline suggested by the instructor so that at a glance one may see the relation of all the data to each other. Erasures should never be made in the notebook; if a mistake has been made it should be crossed out neatly and followed by a new, correct record of the observation or calculation. It is customary to place on the left-hand page of the notebook all calculations involved in the determination and such details as equilibrium points of the balance, and to place on the right-hand page the results of weighings, buret readings, calculations, etc. The material on the right-hand page should always be kept up to date; that is, as soon as a calculation has

been made on the left-hand page the result should be transferred at once to the right-hand page. All computations should be made during the laboratory period and directly in the notebook rather than on odd scraps of paper or on filter paper.

A great deal of time may be saved by keeping busy during the entire laboratory period. For example, while a precipitate is being filtered it is possible to weigh a crucible, or during an ignition to prepare a solution for later use; and almost always there are calculations that may be made while some necessarily slow operation is being carried out. Such time-saving expedients are anticipated by acquiring a thorough understanding of each procedure before starting it.

It should be borne in mind that other people are working in the laboratory and sharing many of the reagents. It therefore is the responsibility of each student to cooperate by exercising care in handling reagents, refilling reagent bottles and replacing all common laboratory property at the right location. A substance removed from its container in greater amount than needed should not be returned to the container since contamination might result.

OPERATIONS

Samples. As a rule samples dispensed in the quantitative laboratory for analysis already have been properly prepared. That is to say they are typical of the complete lot of the material from which they were taken. Moreover, if solid, the material has been ground to proper fineness and often it has been dried. This saves a great deal of students' time and permits a greater number of experiments to be performed than otherwise would be possible. However, unless the beginner has some experience in preparing a sample, it is likely that he will fail to appreciate the cautions necessary in this preliminary step. He should, therefore, give careful attention to the following considerations.

A sample portion, whether it be, for example, from a mineral deposit, a carload lot of solid material, a tank or vat of liquid or a large body of water, almost always should be taken in such a manner as to be as nearly representative of the whole as possible. Thus samples are to be distinguished from specimens, which are usually gathered to illustrate particular features and therefore are not typical of the whole. Sampling is not a casual task and great care and judgment are required to secure a sample for analysis. The chemist should secure his own samples when possible, or supervise their collection; if neither is possible his report should state specifically that the analysis is based on the material as delivered to him.

The method of taking a sample will depend upon the particular conditions. The field geologist, for example, is more interested in the

richness of a given ore not yet mined than he is in the carloads of ore already taken from the mine. On the other hand, the chemist more often is called upon to determine the analysis of the ore which, already taken from the earth, is being purchased by the processor. But in any event it is imperative that utmost care be taken to secure a workable quantity of material which will yield the information wanted. In analyzing a lake of water information about the dissolved oxygen at various depths may be desired; in that case the sampling is a simple matter (given the proper apparatus) of taking the water at the several depths. The same approach is made in taking muck and humus samples. Most commonly, however, it is the sample characteristic of the entire lot which is desired, and since materials like coal, ores and even alloys are not homogeneous, it often is necessary to take a gross sample of perhaps 500 to 1000 pounds by combining "grab" samples taken at random from all parts of the entire mass. As a rule the number of portions should be not less than 20 and the total weight of the gross sample should be at least a hundredth of the entire lot. When the gross sample has been gathered, since it too will not be homogeneous, it must be reduced in particle size and mixed. This is often done by mechanical jaw crushers or a steel hammer and plate, the latter being preferred when possible since it is less likely to introduce foreign material into the sample. After a given operation has reduced the particle size the mixing may be accomplished as follows: The entire quantity is shoveled into a cone, the cone is flattened and the flat, circular mass is quartered and two diametrically opposite quarters are made into a second cone. After further crushing the process is repeated as many times as necessary to yield a proper quantity and particle size, say about 25 to 1000 g. of 10-mesh particles. It may be necessary, if the material is difficult to dissolve, or if a fusion with a flux is to precede solution, to reduce to a still smaller size. The ball mill is the most convenient apparatus for grinding[1] to an extreme state of subdivision, but the agate mortar and pestle usually suffices if the quantity of material is not too large. The small quantities which can be ground at one time in the mortar are combined after they have been pulverized and are thoroughly mixed by placing upon a glazed paper and lifting the corners, one after the other, thus causing the powdered particles to roll over themselves ("tabling"). Finally the fine sample is placed in a bottle and tightly stoppered.

Weighing the Sample for Analysis. The accurate weighing of the sample involves precautions which call for considerable explanation.

[1] Grinding should not be carried out for an unnecessarily long time because foreign substances may be added to the sample from the mill or mortar. Furthermore, excessive grinding may cause the sample to lose water of hydration or otherwise cause a change in composition, particularly from oxidation.

The sample may be weighed either directly or by difference. These points are discussed in the chapter on the balance (p. 39ff).

Solution of the Sample. Whether the analysis is based upon the precipitation and subsequent weighing of an insoluble compound of the constituent sought, or upon the interaction of definite volumes of solutions of the unknown and certain reagents, or upon attributes such as intensity of color, it is first of all necessary to bring the sample into solution. The simplest means of accomplishing this is to dissolve the sample in water. However, many substances are practically insoluble in water. In such cases it frequently happens that treatment with a mineral acid will suffice. Hydrochloric acid of a concentration of about 1:1 with water should be tried first. Hydrochloric acid is a reducing acid but if the sample itself is an oxidizing agent the action may be hastened by adding, along with the acid, a reducing agent like sodium bisulfide. Should the sample contain reducing substances, hydrochloric acid plus potassium chlorate will be more effective. In the case of metals above hydrogen in the electromotive series, hydrochloric acid alone is sufficient for solution; for other metals and for many alloys nitric acid will be best, or aqua regia may be necessary. If the latter treatment fails to dissolve the sample it may be treated with perchloric acid[2] or with hydrofluoric acid and nitric acid in a 2:1 ratio. The latter must be carried out in a platinum crucible and the excess hydrofluoric acid removed by adding 2 or 3 ml. of sulfuric acid and evaporating until sulfur trioxide fumes begin to come off.

It is not necessary to dissolve the entire sample, but only to dissolve the constituent that is to be determined. For example, hot 1:1 sulfuric acid often will dissolve the iron of an iron ore, leaving a sandy colored residue of silica and aluminum silicate. There is no need to bring this residue into solution unless a complete analysis is desired. The color of the residue is usually a satisfactory indication as to whether or not all of the essential constituent has been dissolved, since iron ores are red, brown or black; copper ores are blue, green or black, etc.

Fusions. When the sample resists solution by the above methods it is necessary to fuse the sample with a suitable flux. The purpose of the flux is to convert the sample into compounds which are soluble either in water or in acids. Just what flux is best to use depends upon the nature of the material. Silicates, for example, should be fused with an alkaline flux of sodium carbonate which converts nonmetals into sodium salts and metallic constituents into oxides soluble in acids. On the other hand, many oxide ores, like those of iron and aluminum, require, for complete analysis, an acid flux such as potassium acid sulfate which changes the

[2] Hot concentrated perchloric acid in contact with organic matter should be avoided since such a combination may cause dangerous explosions.

oxides into soluble sulfates. Oxidizing fluxes, consisting of mixtures of sodium carbonate and either potassium chlorate, sodium peroxide or potassium nitrate, should be employed with samples of arsenic ores; reducing fluxes of sodium thiosulfate or of sulfur mixed with sodium carbonate are useful in separating many of the metallic sulfides. As a rule the alkaline fusions should be carried out in platinum crucibles, while nickel crucibles may be used with an acid flux. Silver or iron crucibles are recommended for the oxidixing fluxes. When a platinum crucible is thought proper, consult the instructor before actually starting the fusion.

In any case, the actual fusion is preceded by careful preparation of the sample and flux. The former must be ground to a fine state of subdivision and thoroughly mixed with the flux. A small quantity of the flux alone is put in the crucible, melted and, through a swirling motion, distributed over the bottom and sides of the crucible to three-quarters of its height. The mixed sample and flux are then added, a small additional amount of flux is placed on top of the mix and the crucible then is heated, slowly at first, until fused. After 30 minutes to an hour, the heat is removed and the crucible is rotated while cooling in such a manner that the cake solidifies as a crust over the inside wall of the crucible instead of as a small button in the bottom. When cool, the crucible and contents are placed in a beaker or casserole, covered with water, or with acid if necessary, and warmed until complete solution results.

Evaporation. It is frequently necessary in the course of an analysis to evaporate a liquid in order to reduce its volume, or even to carry the process to dryness. Evaporations are time-consuming and there is not much that may be done to hasten the process. Shallow vessels obviously will give a larger liquid surface and increase the rate somewhat. If the evaporation is to be to dryness it can be carried out overnight. Care should be taken in choosing the type of container to be used. Glass, and to a lesser extent porcelain, is attacked by alkaline solutions, especially as the concentration increases. If highest accuracy is demanded, platinum evaporation dishes are to be preferred. Even with platinum high concentrations of alkaline solutions must be avoided; such solutions should be made faintly acid before evaporating.

Evaporations should be made on a steam bath or on an electric hot plate at a low temperature. The solution should not be allowed to boil since both spattering and bumping may occur. To prevent dust from falling into the dish it should be covered with a watch glass resting on a glass triangle or with the special ribbed watch glass now available which allows for the escape of the vapor.

Digestion. When a precipitate is first formed from a solution its state of fineness is so great that often it will pass through the pores of a filter paper. This difficulty is usually prevented, however, if the particles

of the precipitate are coagulated or if they may be made to assume a larger particle size. The latter condition may be brought about by heating the precipitate and the mother liquor over a steam bath or hot plate for an hour or two, or overnight. The solubility of salts is slightly greater when the solid is extremely finely divided; it follows that a solution which is saturated with respect to the finely divided particles is, at the same time, supersaturated with respect to the larger crystals. As a result, during digestion precipitation will continue upon the coarser particles at the expense of the finest particles and the latter will eventually dissolve. The final result then will be not only the elimination of the finest crystals, and thus a more easily filtrable precipitate, but actually a small decrease in the solubility of the precipitate.

Transfer of Liquids. One of the commonest sources of error for the beginner in the quantitative laboratory results from loss of liquid when it is transferred from one container to another, or to a filter. Yet it is easy to avoid this error simply by developing at once the invariable habit of pouring a liquid down a stirring rod held vertically against the lip of the vessel. In this manner the drop which otherwise would flow from the lip down the outside of the beaker is retained by the rod. One should never swing the rod, with its drop or two of liquid clinging to it, between two vessels. Instead, the rod should always be either in or above one of the vessels (or the filter). The final step in the transfer of liquids should be the rinsing of the original container with three successive portions of the solvent in order to avoid losing the film of solution adhering to the walls of the container. Note that three small rinse portions are better than one larger portion; the principle upon which this statement is based is the same as that which will be discussed later in connection with the use of many small portions in washing precipitates.

Filtering Precipitates. Before a precipitate is weighed it must be freed from impurities. To accomplish this it must be filtered and then washed until both it and the filter are clean. The precipitate is filtered through a filter paper if it is a compound which either will withstand subsequent ignition without changing its composition or is converted completely into a compound of definitely known composition. Filter papers for quantitative work have been treated with hydrochloric and hydrofluoric acids so that they will be "ashless" after ignition. The weight of the ash is marked on the box containing the papers and should be less than 0.1 mg. Filter papers may be purchased which meet various needs. Some will retain finer precipitates than others, but usually the finer the pores of the paper the slower will be the filtration. The paper selected for a given filtration should be chosen with due consideration of the nature of the precipitate.

If the substance filtered is one like silver chloride which cannot be

ignited without decomposition, it must be filtered through a medium other than paper. The Gooch crucible, made either of platinum or of porcelain, is the crucible most frequently used in such instances. It is much like an ordinary crucible except that the bottom is perforated. A "soup" of asbestos suspended in water is poured into the crucible and suction is applied (Fig. 1) so that a mat about as thick as a dime is packed down upon the perforated bottom. Then a perforated disk is placed upon the mat and more asbestos is poured in upon it. After suction again is applied the result is a mat about twice the thickness of a dime with the disk sandwiched in between the two layers. Under moderate suction water should drip through the crucible; if it streams through, the asbestos is too thin and should be replaced with a thicker mat.

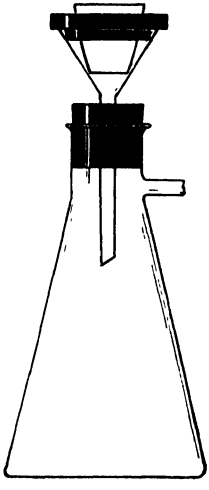


FIG. 1. Gooch crucible and suction flask.

Porous porcelain crucibles and sintered glass crucibles are often used instead of Gooch crucibles. In both cases the bottom of the crucible is sufficiently porous to function as a filter. Suction is applied in the same manner as with a Gooch crucible.

Washing Precipitates. Since the precipitate is always formed in the presence of the ions of the supernatant liquid it is necessary that thorough washing follow the filtration. The time expended in washing is shortened if the precipitate is first washed by decantation. After the precipitate has settled in the beaker, almost all of the liquid is passed through the filter while the precipitate largely remains in the beaker (Fig. 2). Then wash solution (or water) is added and agitated with the precipitate. The precipitate is allowed to settle and the liquid is again poured off into the filter. Wash solution is added to the beaker a second time and stirred, the precipitate allowed to settle and the new supernatant liquid decanted into the filter as before. After this operation has been repeated three or four times the entire precipitate is transferred to the filter in a manner illustrated in Fig. 3, that is, by placing the stirring rod across the top of the beaker and holding over the filter as illustrated, after which a stream of water or wash solution is directed into the beaker so that the entire inside of the beaker is washed free of precipitate. If any particles of precipitate adhere to the beaker it may be necessary to detach them with a policeman (a glass rod equipped with a rubber tip). In this case both beaker and policeman must be flushed again with water which goes thence into the filter.

Often it happens that a filter, while showing no leakage during the filtration, will not retain the finest particles of the precipitate after the

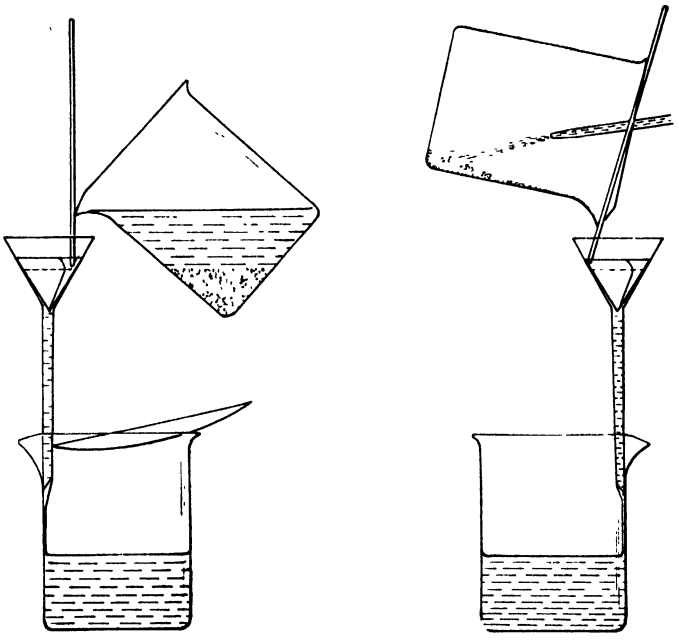


FIG. 2. (*Left*). Decanting a liquid from beaker to filter.
FIG. 3. (*Right*). Flushing precipitate from beaker to filter.

washing has been continued to the point where the precipitate is practically clean. This happens because, so long as the precipitate was not clean, there were sufficient ions present to prevent any particles from approaching the colloidal state, but just as soon as the precipitate is virtually clean there are no longer enough ions to cause flocculation; as a result some precipitate may leak through the filter. This peptization can be prevented by washing with a dilute solution of a suitable electrolyte instead of with pure water. The electrolyte used must be one that may be removed by volatilization during the ignition of the filter paper. Thus dilute acids, ammonium hydroxide or ammonium salts are commonly employed. Because of the possibility of peptization when washing with water it is a good idea to replace the beaker receiving the filtrate with another empty beaker just before the final stages of washing. Then, if leakage does occur, the volume to be refiltered will not be so large. (See p. 240.)

The washing of a precipitate must be continued until a test on a few milliliters of the filtrate which has just filtered through reveals no presence of contaminating ions. During washing it is advantageous to fill the filter about three-quarters full of wash solution and allow this to drain practically completely before refilling to the three-quarters level. Rapid cleansing is also promoted if the wash solution is played into the filter so that the

whole of the precipitate is agitated; care should be taken, however, to avoid spattering.

Subdivision of Wash Liquid. It has been mentioned already that in rinsing following the transfer of liquids from one vessel to another, and in washing precipitates, it is better to use many small portions of the liquid than to use a few large portions. After the addition of wash solution the quantity of contaminant in the solution still clinging to the precipitate, for example, may be calculated as follows:

Let W be the milliliters of contaminating solution adhering to the precipitate and let L be the milliliters of wash solution available for each washing operation. Let C_0 be the concentration of the contaminant in g./ml. in the original W milliliters, and C_1, C_2 . . . C_n be the concentrations of the substance adhering to the precipitate after the first, second . . . nth washings.

After the first washing the concentration of the contaminating substance in the liquid adhering to the precipitate is obviously

$$C_1 = \frac{W}{W + L} \cdot C_0 \tag{1}$$

and following the second washing with another L ml.

$$C_2 = \frac{W}{W + L} \cdot C_1 \tag{2}$$

Substituting the value of C_1 from equation (1) into equation (2),

$$C_2 = \frac{W}{W + L} \cdot \frac{W}{W + L} \cdot C_0 = \left[\frac{W}{W + L}\right]^2 C_0$$

and, similarly, after n washings

$$C_n = \left[\frac{W}{W + L}\right]^n C_0 \tag{3}$$

For example, suppose that 1 ml. of the supernatant liquid adheres to the precipitate after filtering and that the concentration of the objectionable ion is 1 g./ml. Assume that the washing were done with one portion of wash liquid of 50 ml. volume. In this case the concentration of the solution clinging to the precipitate would be

$$C_1 = \left[\frac{1}{1 + 50}\right]1 = \frac{1}{51} = 2.0 \times 10^{-2}\ \text{g./ml.}$$

whereas if the wash liquid consisted of the same total volume of 50 ml. but was divided into five portions of 10 ml. each, and these were successively used,

$$C_5 = \left[\frac{1}{1 + 10}\right]^5 1 = \left[\frac{1}{11}\right]^5 = 6.2 \times 10^{-6}\ \text{g./ml.}$$

The increase in efficiency is therefore

$$\frac{2.0 \times 10^{-2}}{6.2 \times 10^{-6}} = 3200 \text{ fold.}^{3}$$

PROCESS OF EXTRACTION

The rule of many small portions of wash liquid in preference to few large portions is similar to the principle involved in the process of extraction. Sometimes it is expedient to recover a certain solute from an aqueous solution, for example, by shaking the water solution with an immiscible (usually organic) solvent in which the solute is much more soluble than in water. The ratio of the solubilities of the solute in the two solvents is the theoretical distribution constant. To illustrate, a substance might dissolve to only half the extent in one solvent as in another; the distribution constant would have a value of 0.5 and if equal volumes of the two solvents were shaken with a given weight (not exceeding the total solubility) of the solute there would be, after the two liquid layers separated, one-third of the solute in the one liquid and two-thirds in the other. ($K = \frac{1}{3} \div \frac{2}{3} = 0.5$.)

The mathematical proof of the advantage of using many small portions of the extracting liquid is developed as follows:

Let W ml. of a solution containing X_0 g. of solute be treated repeatedly with L ml. of extractant. Following the first extraction let X_1 be the grams of solute remaining unextracted. If K is the distribution constant (defined as the ratio of the solubility in the extracted phase divided by the solubility in the extracting phase), it may be evaluated thus[4]:

$$K = \frac{X_1/W}{(X_0 - X_1)/L} \tag{4}$$

and solving for X_1,

$$X_1 = KW \cdot \frac{(X_0 - X_1)}{L} = X_0 \cdot \frac{KW}{KW + L} \tag{5}$$

After the second extraction

$$X_2 = X_1 \cdot \frac{KW}{KW + L} \tag{6}$$

Substituting in (6) the value for X_1 found in (5),

$$X_2 = X_0 \cdot \frac{KW}{KW + L} \cdot \frac{KW}{KW + L} = X_0 \left[\frac{KW}{KW + L}\right]^2 \tag{7}$$

or, in general,

$$X_n = X_0 \left[\frac{KW}{KW + L}\right]^n \tag{8}$$

From equation (8) we may calculate the weight of solute remaining unextracted after any number of operations. Suppose a liter of aqueous solution containing 10 g. of a solute were extracted with a liter of an immiscible solvent, and assume that the value of K is 0.5. If the whole liter of extractant were used at once the

[3] Assuming that thorough agitation has been established in each operation and that there are no complicating factors, e.g., adsorption.

[4] Taylor, *Treatise on Physical Chemistry*, D. Van Nostrand Co., New York, 1931, pp. 485–87.

value of X_1 would be

$$X_1 = 10\left[\frac{0.5(1000)}{0.5(1000) + 1000}\right] = 3.33 \text{ g.}$$

On the other hand, if two portions of extractant of 500 ml. each are successively used, $X_2 = 2.5$ g. Subdivision into ten 100 ml. portions yields $X_{10} = 1.6$ g. It is evident then that the use of many small portions is of much advantage. When K differs widely from unity, as usually is true, the advantage is much more marked than in the example cited.

Equation (8) is often employed to calculate the efficiency of extraction when L ml. of extracting liquid is to be repeatedly used. In such a case the total volume of extractant would approach infinity as n became infinitely great; at the same time X_n would approach zero as a limit. This situation, while theoretically interesting, should be distinguished clearly from the practical situation which always deals with a finite quantity of extractant. This limited amount of extractant, as the numerical example already given shows, should be subdivided into many small portions of L/n ml. each. When the total quantity of extracting liquid, L, is limited, so also will be X_n, the amount of solute remaining unextracted. We may emphasize the distinction if instead of equation (8) we write

$$X_n = X_0\left[\frac{KW}{KW + L/n}\right]^n. \tag{9}$$

It has been shown[5] that here the limit of X_n, as n approaches infinity, is not zero but proves to be $e^{-L/KW}$. The point has sometimes been overlooked in extraction work that it is impossible, when a definite quantity of extractant is used, to approach 100 per cent efficiency; that, no matter how great the subdivision of the extractant may be, a portion, namely, $e^{-L/KW}$, of the solute originally present in the W ml. of solution cannot be removed. This has been experimentally demonstrated in a number of extraction studies by von Saaf.[6] In brief, equations (8) and (9) show, when we solve for the limiting values, that repeated extraction with L ml. portions would lead to the use of an infinite total quantity of extractant, and in this case the amount of unextracted solute approaches zero as a limit; but when a finite total quantity of extractant, L ml., is subdivided even into an infinite number of infinitesimally small portions, the amount of unextracted solute approaches a finite value as a limit, namely, $e^{-L/KW}$.

Igniting Precipitates. After a precipitate has been filtered and washed clean it must be dried before weighing. When a Gooch or other filter crucible has been employed it is customary to put the crucible in a beaker and then place in a constant temperature oven at a suitable temperature, usually around 105° to 120°. The crucible may be placed in a muffle furnace, provided the temperature is not so high as to cause an indefinite change in the composition of the precipitate. If a filter paper has been used it is the usual practice to ignite the paper and precipitate before the weighing. Certain cautions must be observed. Although many analysts transfer the wet filter paper with the precipitate directly to the crucible for ignition, it is safer first to dry the filter paper somewhat by placing

[5] Griffin, *Ind. Eng. Chem., Anal. Ed.*, **6**, 40 (1934).

[6] Griffin and von Saaf, *Ind. Eng. Chem., Anal. Ed.*, **8**, 358 (1936).

the funnel vertically in the oven at 105° for 10 or 15 minutes. The paper and precipitate may then be removed with less danger of losing any precipitate than when wringing wet. After the filter is removed from the funnel it is carefully pressed flat, the corners turned in and the top folded over so that the precipitate is completely enveloped. The bundle is then transferred to the crucible, which has previously been weighed to a constant weight, and the ignition is begun. A triangle of clay or platinum holds the crucible. The lid is placed on the crucible and heat is applied from a small flame of the burner. After a few minutes the contents of the crucible are quite dry and the paper should soon begin to char; if it does not, a slightly higher flame should be used. As a rule the charring should require about 15 minutes. Should the paper begin to flame the burner must be removed at once so that the flame is extinguished. When no more smoke is observed the crucible is tilted and the cover partly removed as seen in Fig. 4. The flame is now elevated but only the blue oxidizing portion of the flame should touch the crucible. After about half an hour all of the carbon should have disappeared and the crucible and precipitate are ready to be cooled.

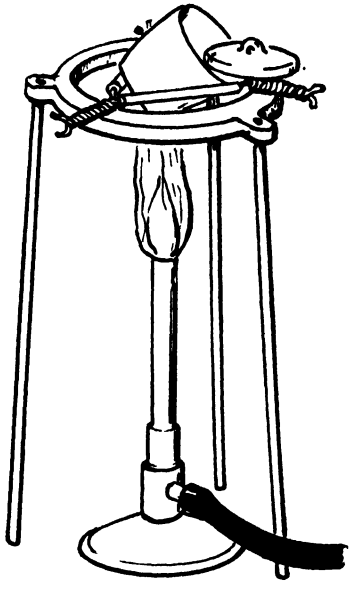


FIG. 4. Ignition of filter paper and precipitate.

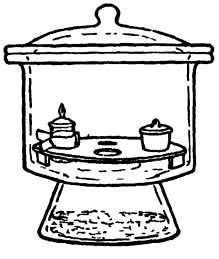


FIG. 5. Desiccator containing weighing bottle and crucible. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

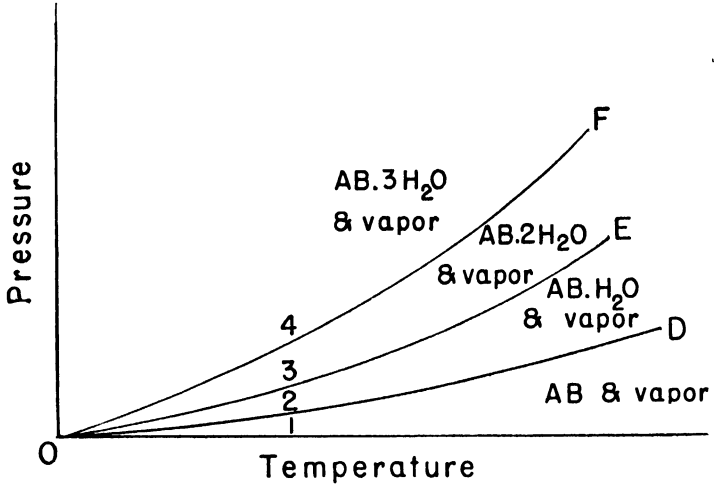
Use of the Desiccator. After the ignition the crucible is transferred with tongs to a desiccator to cool. If allowed to cool in air, considerable moisture would be taken up. The desiccator (Fig. 5) provides an atmosphere which should be of constant and low humidity. After not less than 20 minutes, nor much more than an hour, the crucible is removed from the desiccator and weighed. It then is heated again for the same period as the first ignition and again cooled and weighed. The ignition, cooling and weighing must be repeated until two successive weighings agree within 0.3 mg. Then and then only may the crucible and contents be said to be dry and of constant weight.

It should be realized that no desiccant is a perfect drying agent, although some, like phosphorus pentoxide and magnesium perchlorate, are nearly so. The

most commonly employed desiccants are anhydrous salts which, when they function as drying agents, take up moisture to form hydrates. Exactly what happens when a moist object is placed within a desiccator containing an anhydrous salt as a desiccant may be understood most clearly from the standpoint of the phase rule[7] which states that

$$P + F = C + 2$$

where P is the number of phases (gas, liquid, solid) present in a system at equilibrium; C is the number of components (the smallest number of individually variable constituents mathematically defining the composition of each phase); and F is the number of conditions, usually only temperature, pressure and composition, which may be varied without causing a change in the number of phases.



Schematic drawing of vapor pressure curves for a hydrated salt.

Suppose that we have a salt, AB, which may form the three different hydrates, $AB.H_2O$, $AB.2H_2O$ and $AB.3H_2O$. What relation exists between the salt and the moisture in the atmosphere of the desiccator? The anhydrous salt may exist in contact with water vapor within certain limits of temperature and pressure without the formation of any hydrate whatsoever, even the lowest hydrate. The accompanying drawing shows the pressure-temperature relations which must hold under varying conditions. It shows an area for the bivariant equilibrium, AB + vapor; here both pressure and temperature may be varied simultaneously, within limits, without a change in the number of phases. That is, $F = C + 2 - P = 2 + 2 - 2 = 2$, for we have two components, salt and water, and the two phases, solid and gas. If the vapor pressure is sufficiently increased (as when a moist object is placed in the desiccator) a point is finally reached at any given temperature where the lowest hydrate, $AB.H_2O$, begins to form. When this happens there are three phases present: AB, $AB.H_2O$ and vapor. Therefore $F = 2 + 2 - 3 = 1$ and the system is univariant; the pressures and temperatures for this equilibrium are represented by curve OD which is called the dissociation curve for the mono-

[7] For the derivation of the phase rule see any text on physical chemistry.

hydrate, $AB.H_2O$. Similarly there is a dissociation curve for each of the other two hydrates, curves OE and OF. The areas between these curves all represent regions where bivariance prevails; only along the curves themselves do we have univariance.

To return to a consideration of dehydrating efficiency: it is obvious that if the desiccator contains anhydrous AB at a given temperature, 1, and a moist object is placed in the atmosphere above the desiccant, nothing will happen provided the moisture present is not enough to create at least pressure 2, and the desiccant will take up no vapor at all. If sufficient moisture is present initially to cause a pressure as great as or greater than point 4, the extent to which the pressure is reduced will depend upon the ratio of the quantity of salt to the quantity of vapor. If the amount of salt be just enough so that all of it is converted to $AB.3H_2O$ the pressure established will be that of point 4; if it is so much that all of the vapor taken up goes into the formation of $AB.H_2O$ and no higher hydrate, then the pressure will fall to 2. Under no condition can the pressure fall to zero, save only if the temperature were absolute zero.

Obviously when a dry object (for example, a crucible which has been heated to a high temperature) is placed in the desiccator we are not surrounding the crucible with a "dry" atmosphere. The desiccant immediately after being placed in the desiccator consists of anhydrous salt plus at least some of the lowest hydrate, $AB + AB.H_2O$, and for these two to coexist along with vapor demands, *at a given temperature*, no degree of freedom. This means that one pressure and one only can prevail—namely, pressure 2, in the diagram. The dry crucible therefore, as it cools, will begin to take up moisture and actually gain weight. Because of this, objects should never be allowed to remain in a desiccator indefinitely. An hour is the maximum time and 20 minutes is enough. That constant weights of objects can be obtained at all is due to the fact that the rate of cooling is fast and the rate of phase equilibrium is relatively slow as a rule. Thus the object is cool before it has had time to reach phase equilibrium with the atmosphere in the desiccator (which, in turn, is in equilibrium with the desiccant), that is to say, before it has taken up all of the moisture which it would, given time. This emphasizes why it is important not only to avoid an unduly long period for cooling in the desiccator but always to allot approximately the same length of time for cooling when weighing to a constant weight.

Aside from the above theoretical considerations it is important to observe the practical precaution of keeping the cover on the desiccator at all times except when transferring an object to or from it. Even then the cover is removed and replaced as quickly as possible in order to reduce to a minimum the amount of moist air admitted from the atmosphere.[8] Furthermore the cover should always be kept greased with petrolatum or, preferably, stopcock grease.

VOLUMETRIC INSTRUMENTS

The subdivision of analytical chemistry known as volumetric analysis deals largely with the measurement of volumes of solutions. The instruments commonly employed in this type of work are the graduated cylinder, the volumetric flask, the pipet and the buret. The cylinder is used only for approximate measurements of volume; the last three are used

[8] Booth and McIntyre, *Ind. Eng. Chem., Anal. Ed.*, **8**, 148 (1936); Hillebrand, *U.S. Geol. Survey, Bull.* 422, p. 119 (1910).

when exact quantities of liquid are desired. Volumetric instruments are made either to contain or to deliver a certain volume. As a rule volumetric flasks belong to the former class while burets and usually pipets are of the latter type. The question of exactness in measuring volumes will be explained further in the chapter on calibrations but it may be pointed out at once that great care must be exercised in properly handling these pieces of apparatus if correct measurements are to be attained.

Volumetric Flasks. The volumetric flask (Fig. 6) is a somewhat pear-shaped glass vessel having a long narrow neck. It may or may not be fitted with a ground-glass stopper. On the neck will be found an etched ring which indicates the level to which it must be filled with a liquid in order to contain the volume marked on the body of the flask at the temperature indicated. When the flask is used to make up a definite volume of a solution the proper weight of solute must be dissolved in a small quantity of the solvent in a beaker; the solution then is poured down a stirring rod from the beaker into the flask. The beaker is rinsed several times with the solvent and the rinse is carefully added to the flask. More solvent then is added to the flask until almost to the neck, after which the flask is whirled, care being taken not to wet the neck above the calibration mark. The solution then is allowed to attain room temperature, which should be within two or three degrees of that for which the flask is calibrated, after which solvent is added until the meniscus is tangent to the mark. The flask then is stoppered and the solution thoroughly shaken.

Sometimes a volumetric flask bears two marks, the upper one for delivery and the lower one for content. When used to deliver, flasks should be emptied by gradually inclining so that a continuous stream results, and should be held finally in a vertical position for 30 seconds to allow for drainage. Then the mouth of the flask should be touched to the receptacle to remove the hanging drop.

Pipets. A pipet (Fig. 7) is a narrow tube with a bulb near the middle. The bulb has a capacity slightly less than the volume indicated on the pipet. An etched ring on the tube above the bulb marks the level for the liquid in order that the pipet shall deliver (transfer pipets) the volume specified. (Mohr pipets do not have the bulb but consist of a straight tube usually graduated in tenths of milliliters.)

A pipet is used in the following manner: After cleaning the pipet thoroughly[9] it is rinsed at least three times with the solution to be

[9] To test for cleanliness fill the instrument with distilled water and let drain into a beaker. Examine carefully. If any droplets cling to the inside surface the instrument is not clean. Cleaning solution is prepared by dissolving 30 g. of sodium dichromate in a liter of concentrated sulfuric acid. The solution may be used slightly warm when cleaning volumetric apparatus, but never hot, since this causes the glass to expand and unless an equal contraction takes place upon cooling the capacity of the instrument will be altered.

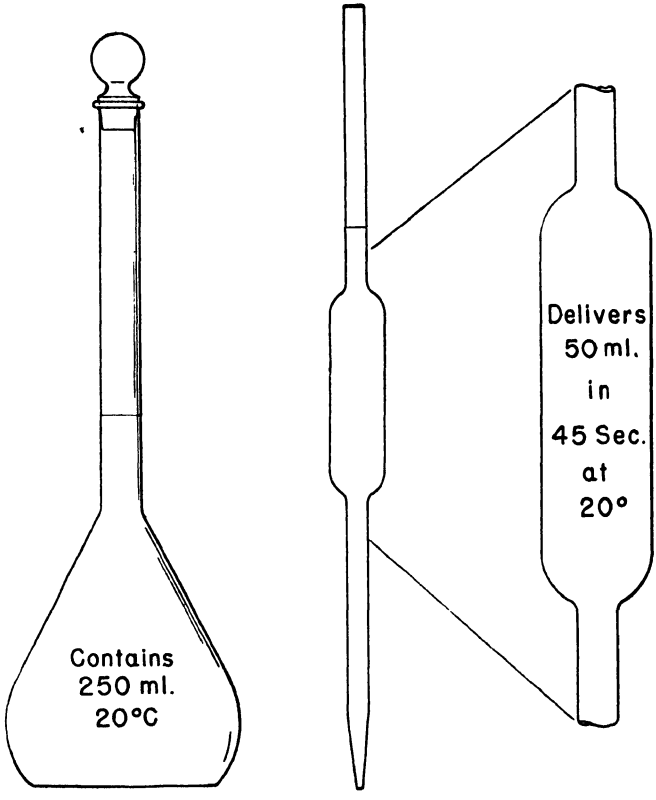


FIG. 6. (*Left*). Volumetric flask.
FIG. 7. (*Right*). Pipet.

measured. This is done by drawing small portions into the pipet through suction applied by the mouth to the upper end of the pipet. The pipet is held in a horizontal position and rotated so that the whole inside surface is wetted with the solution. The rinsings are discarded. The definite volume of solution now may be measured by filling through suction to a point above the graduation. Then the forefinger is quickly placed over the top of the tube so that the liquid is held in the pipet. The pipet is now held over a spare beaker and a little air is admitted by carefully releasing the pressure of the finger. When the level of the liquid is tangent to the mark (viewed in a line horizontal with the eye), the hanging drop is gently tapped off by bringing in contact with the spare beaker. The pipet then is held vertically over the receiving vessel and the contents allowed to drain. About 15 seconds after the flow ceases the tip should be touched to the surface of the vessel. The small quantity of liquid remaining in the tip should not be blown out.

Burets. Burets (Fig. 8) are used in volumetric analysis in the operation known as titration. In a titration the solution is run from the buret into a vessel where a chemical reaction takes place. The flow from the buret is stopped when chemically equivalent quantities of reactants have been brought together. Thus the stoppage may occur at any volume and burets accordingly are usually marked in tenths of milliliters. A buret should be cleaned thoroughly[10] and rinsed three or four times with the

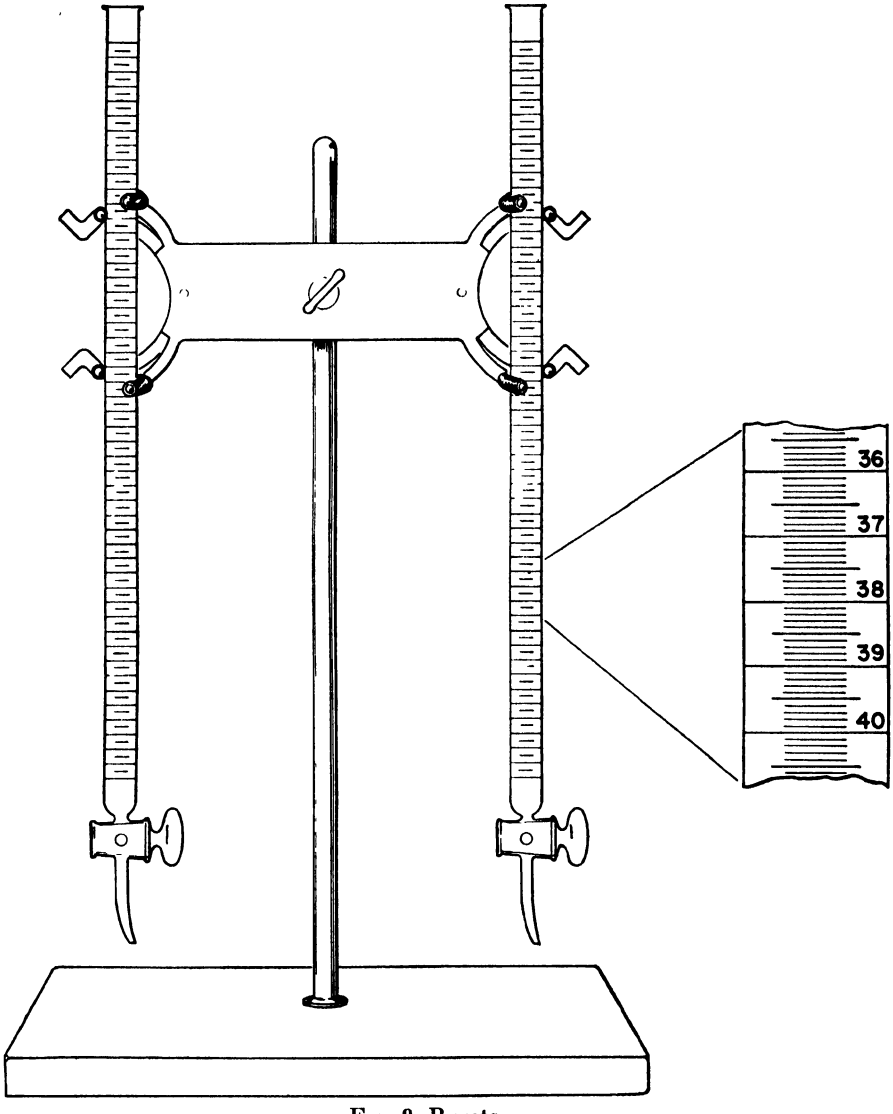


FIG. 8. Burets.

[10] See footnote 9, p. 18.

solution with which it is to be filled in the same manner as was described for the pipet. It is then filled, and by withdrawing solution into a spare beaker the meniscus is allowed slowly to approach the zero mark. There must be no air bubble in the tip and any hanging drop must be removed. When the buret is used it should be clamped in a vertical position and when the flow of liquid has ceased the hanging drop must be removed by touching the tip with the inside surface of the receiving vessel. The volume reading should not be taken until 30 seconds after the outflow has stopped in order to allow for drainage.

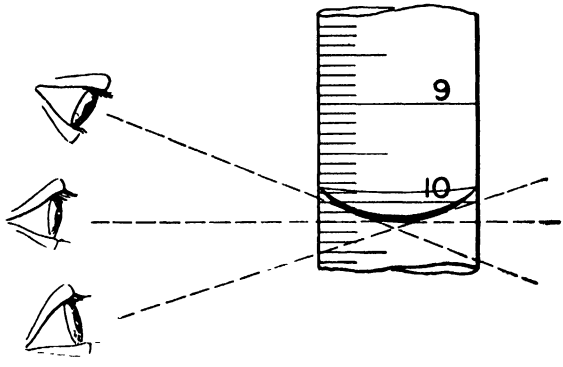


FIG. 9. Parallax. Only when the eye is on a level with the meniscus will the reading give no parallactic error.

Parallax. When using volumetric apparatus the lowest point of the meniscus should be taken for the reading except in cases where the meniscus is not observable, as, for example, with permanganate solution. In such a case the upper periphery is taken for the reading. In any reading it is imperative to avoid errors of parallax by viewing the instrument with the eye on a level with the meniscus. If the etched line extends more than halfway around the instrument the eye is on a level with the graduation mark if the front and back of the mark are coincident. It is evident from Fig. 9 that if the eye is too high the reading will be too high, and vice versa.

Questions and Problems

1. Name several examples of instances when the sample taken for analysis should not be representative of the whole body of material.
2. What objections are there to excessive grinding when reducing the particle size of a sample of material for analysis?
3. Discuss the steps necessary to obtain a sample, suitable in size and in degree of fineness for analysis, from a carload of coal.
4. Name the fluxes most commonly used for converting acid-insoluble substances into soluble form.

5. Explain how the digestion of a precipitate will result in a larger particle size of the "insoluble" substance.
6. Why are the "ashless" filter papers used in quantitative work more expensive than the filter papers used in qualitative analysis?
7. Explain why a precipitate which has been filtered does not leak through the paper until it has been washed clean with water, but then may begin to run through. How may the leakage usually be prevented?
8. Prove mathematically that in washing a precipitate the subdivision of a given quantity of wash liquid into many small portions which are used successively increases the efficiency of the washing.
9. What is the objection to leaving a dried object in a desiccator for a long time—for example, overnight—before weighing? Explain fully.
10. Which has a greater capacity, a 250 ml. volumetric flask marked "to deliver" or a 250 ml. volumetric flask marked "to contain"? Explain.
11. What is the best method of testing a buret for cleanliness?

Chapter 3

ACCURACY, PRECISION, ERRORS AND SIGNIFICANT FIGURES

THE PURPOSE in making any observation or measurement is to learn the truth about the magnitude involved. Except by accident this may never be wholly realized, and even if it were we would be ignorant of the fact. Exactly what distance separates two points, X and Y? One may apply a measuring stick to ascertain the distance. The experimenter may check himself by making the measurement several times. Each time he will get a somewhat different result. His results will be more concordant the more careful he is in laying off the lengths of the ruler time after time; furthermore, they will be better if his eyesight is good than if not. Another individual may repeat the measurement and the results may more or less coincide with those of the first observer but, except by accident, will not exactly duplicate them. It is evident also that both observers will of necessity fail to perform a good job if the measuring stick is not accurate. It follows therefore that as far as truth is concerned we cannot surely know the distance between points X and Y. What we can do is to procure the best measuring stick possible, check that stick against some standard linear measure which is thought to be highly dependable, work at a constant temperature, have several persons carefully make the measurement, eliminate any arithmetical errors of computation (here only addition) and finally take an average of these several determinations. In all probability then this average or mean should be close to the truth regarding the distance between X and Y. But actually no one ever can say that this or that result, or that the mean of several measurements, is the truth, i.e., that the error is zero. The most of which we can be certain is that we have in our mean an approximation which, because of all the precautions taken, closely approaches the truth.

It must be realized at once that because two or more determinations of the same quantity check one another closely we have no guarantee of small error. If the meter stick with which a certain distance is measured is, say, actually 100.1 cm. in length, erroneous results inevitably must be obtained regardless of the fact that duplicate measurements may agree closely with one another. This points up the distinction between the terms precision and accuracy.

Precision and Accuracy. Precision may be defined as the narrowness of the limits between which it is thought the true value lies. It is a measure of the agreement between two or more determinations of a given quantity. On the other hand, accuracy, a term sometimes mistakenly used interchangeably with precision, denotes the concordance between the result of a measurement and the true value of that measurement. Strictly speaking, since the true value is unobtainable with absolute certainty, this concordance cannot be gaged. Nevertheless, with proper care and proper instruments the true value of a measurement may be obtained within such a small possible span of error that one may assert that the overwhelming *probability* is that the true value lies within a narrow range of which the reported value is the mean.

Obviously if the same error is made to about the same extent in duplicate determinations, the precision would be high while the accuracy would be low. Accurate results are necessarily precise but precise measurements may or may not be accurate. By custom, precision is expressed in terms of deviation (usually in parts per thousand) from the mean of the several determinations; accuracy is *estimated* in terms of error, i.e., departure from the true value.

Practically speaking, accuracy may often be attained (the truth be expressed) if the precision attempted is not too high. To illustrate: The distance between X and Y might be measured by a number of able persons with a steel meter stick which has been calibrated to the millimeter by the Bureau of Standards. Precautions such as regarding the temperature of the surroundings and computing the consequent correction for expansion of steel are made. If an average result of 33.52 m. is reported, the overwhelming probability is that this is the truth; it is accurate. It is hardly reasonable to think that the true value differs from 33.52 m. by more than 1 cm. under the circumstances, particularly if all of the several determinations fell within, say, 0.005 m. of the average value, and if, furthermore, the greatest estimated error due to all possible sources adds up to less than 0.005 m.

If a somewhat careless determination were made in triplicate by another person with results of 34.11, 34.12 and 34.32 m., we conclude that his average of 34.18 m. is somewhat precise but not very accurate. The precision is computed as follows (note that the sign of the deviation is ignored):

	Results	*Deviations from Mean*
	34.11	0.07
	34.12	0.06
	34.32	0.14
3	102.55	3 | 0.27
Mean	34.18	0.09

The absolute mean deviation of a single measurement is 0.09 in a total of 34.18; the relative deviation is

$$0.09:34.18 = X:1000$$
$$X = 2.6 \text{ parts per } 1000$$

The accuracy of the above determination may be said to correspond to an absolute error of $34.18 - 33.52 = 0.66$ m. This would be, in relative terms, 20 parts per 1000. The precision in this case is over seven times the accuracy. Precision then measures the reproducibility of measurements while accuracy indicates the approach to the actual correctness or truth.

Errors

Though no one may hope to attain absolute perfection in making measurements, it is profitable to learn as much as possible about the types of errors likely to occur so as to be in a position to reduce their effect to a minimum. Errors are often divided into two classes: determinate errors and indeterminate (accidental) errors.

Determinate Errors. These are the errors which persistently recur from one determination to another. Their magnitude thus can be estimated fairly well and corrections for them applied. If the error is of the same magnitude time after time (as, for example, would result from the repeated use of a weight supposedly 50.0000 g. which actually was 50.0011 g.) it is called a *constant* error. Often the direction and the degree of this type of error are known and appropriate corrections may be applied. Among the common determinate errors the following may be listed:

1. Instrumental errors, the result of poor construction of apparatus, faulty calibration of weights or volumetric apparatus, impure reagents, etc.

2. Personal errors, the result of idiosyncrasies of the individual, such as inability to note color changes sharply in persons whose sense of color is poor. Such errors usually are constant both in degree and direction. Under this heading comes the not uncommon error of matching colors of a given indicator in titrations or in colorimetric determinations, even in persons whose eyesight is perfect but who are prejudiced by the hue of color obtained in a previous determination. If a certain depth of color has been obtained in the first experiment, it is easy to convince oneself, if the buret reveals a reading slightly lower for the duplicate determination, that one or two more drops of reagent are needed in order to match exactly the color first obtained. Such prejudices can be eliminated by deciding definitely about the color before taking the reading.

3. Methodic errors, which come about for various reasons, all having to do with problems inherent in the method of analysis, from the

sampling (which theoretically can seldom be perfect) on through to the final operation. Practically all analytical methods have their own characteristic inherent errors. These are the most serious of all errors for they can be eliminated or minimized only through working out a different procedure. Other methodic errors may be due to failure of a reaction to take place quantitatively, coprecipitation, slight solubility of precipitates in gravimetric determinations, inability to dry a precipitate completely and the like.

At least some methodic errors may be minimized by better technique. For example, there are usually means of diminishing coprecipitation. Errors due to solubility will be less if, in washing precipitates, one uses the proper wash solution and in the smallest, yet sufficient, quantity. In any event careful attention to the possible type and probable magnitude of these errors is the responsibility of the analyst.

Indeterminate Errors. These errors are "accidental" in the sense that they occur for no apparent cause even when the determination is carried out by a competent analyst and under conditions which are thought to be invariable. The perspicacity of the analyst is of no avail in the case of true, indeterminate errors, and the theory of probability is used to cope with them. In spite of the fact that corrections to counteract the effect of accidental errors cannot be applied it is possible to arrive at an intelligent conclusion regarding what is the "best" number to represent the result in a series of measurements. If an infinite number of observations were made the frequency of the occurrence and the magnitude of the accidental errors may be expressed by the probability law. The frequency of the occurrence Y, of an error of magnitude X, is given by the equation,

$$(1) \qquad Y = \frac{h}{\sqrt{\pi}} e^{-h^2X^2}$$

where Y = frequency of the occurrence of the deviation
X = magnitude of a deviation of frequency of Y
h = a constant the value of which depends upon the character of the measurements (thus its value is the same only for a given kind of measurement)
e and π = constants, 2.718 . . . and 3.141 . . . , respectively.

The curve represented by this equation is called the *probability curve* or the *error curve* and is shown in Fig. 10. Three conclusions are readily drawn from the qualitative nature of this curve: small errors occur more often than large ones; very large errors are very unlikely; and positive

errors and negative errors of the same magnitude are equally likely. Thus in a series of reliable measurements it follows that the value most closely approaching the true value will be one such that the sum of the differences between it and the larger individual measurements will be equal to the sum of the differences between it and the smaller individual measurements. Such a value is called the *arithmetic mean.*

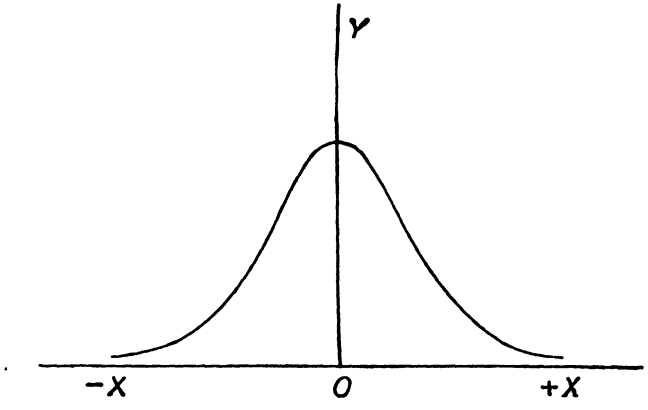


FIG. 10. The probability (error) curve. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

Average Deviation of a Single Measurement. The validity of a given single measurement may be expressed in terms of the magnitude of the deviation that probably attaches to it. This is simply the average of the several differences between the individual measurements and their arithmetic mean, or

$$\text{(2)} \qquad \text{Av. d.} = \frac{|d_1| + |d_2| + \cdots |d_n|}{n}$$

where d_1, d_2 . . . d_n are the individual deviations from the mean.

Average Deviation of the Arithmetic Mean. This term should be distinguished from the above. The average deviation of a single measurement is suitable to give us an estimate of precision as was done in a previous illustration (p. 25). It tells us the average extent by which the several individual determinations differ from their mean. But to what probable extent is this mean itself subject to error; that is, how greatly does it probably depart from the truth?

Before answering this question let us realize that if we take the mean of a few measurements we have a less reliable approximation than if we take the mean of many measurements. It may be shown by the Method

of Least Squares that the reliability of the arithmetic mean of a series of n measurements is $\sqrt{n}$ times as reliable as a single measurement. For example, the mean of 16 measurements is 4 times as reliable as a single measurement and that of 4 measurements is twice as reliable as one measurement. If we designate the error of a single measurement by u, then the error of the arithmetic mean of n measurements is $u/\sqrt{n}$, and the error involved in the arithmetic mean of 4 individual measurements is obviously twice as great as that involved in the mean of 16 measurements.

To come back to the earlier question, we may say then that the arithmetic mean is probably in error to an extent which is $1/\sqrt{n}$ as great as the average deviation of a single measurement, or

$$\text{(3)} \qquad \text{Av. Dev. of Arith. Mean} = \frac{\text{Av. d.}}{\sqrt{n}}$$

Thus if 16 measurements gave a mean of 0.10126 and an average deviation for a single measurement of 0.8 part per 1000, then the average deviation of the arithmetic mean would be $0.8/\sqrt{16} = 0.2$ part per 1000. This means that the value of 0.10126 is possibly in accidental error by 0.00002 or that the true value should be not less than 0.10124 nor greater than 0.10128.

Standard Error. There are still other ways of expressing errors. The *mean error of a single measurement*, often called the *standard deviation of a single measurement*, is defined[1] as the error the square of which is the mean of the squares of the individual deviation from the arithmetic mean, without regard to sign, or

$$\text{(4)} \qquad \text{Stand. Dev. of Single Measurement} = \sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n}}$$

The above, of course, is rigorously valid as a limiting value for an infinite number of observations; if the number of measurements is small a closer approximation of the standard deviation may be calculated by using $n - 1$ instead of n in the denominator under the radical, i.e.,

$$\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n - 1}}$$

Probable Error. The *probable error of a single measurement* is that error of such magnitude that in an infinite number of measurements the number having larger errors than it will be equal to the number having smaller errors than it. The equation for the probable error is

[1] But see Razim, *J. Chem. Education*, **19**, 411 (1942).

(5) Probable Error of a Single Measurement

$$= 0.67\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n-1}}$$

When $n = \infty$ the relation between the three measures of unreliability are:

Av. Dev. = 0.8 Mean (Standard) Error = 1.18 Probable Error

It will be recalled that the expression giving the average deviation of a single measurement, namely, equation (2), if divided by $\sqrt{n}$, yields the average deviation of the mean. Similarly, by dividing equations (4) and (5) by $\sqrt{n}$ we obtain, respectively,

(6) Stand. Dev. of Arith. Mean (Mean Error of Arith. Mean) $= \sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n}} \Big/ \sqrt{n}$

(7) Probable Error of Arith. Mean $= 0.67\sqrt{\frac{d_1^2 + d_2^2 + \cdots d_n^2}{n-1}} \Big/ \sqrt{n}$

The application of these six forms may be illustrated by the following example. It should be remembered, however, that any equation based upon the Probability Law presupposes a large number of measurements, and that with a small number these equations do not command the rigor attained if the calculations could be based upon an unlimited number of observations.

Problem. The results of three measurements were: 55.09, 55.14 and 55.15. Calculate (A) the average deviation, (B) the standard deviation and (C) the probable error of a single determination, and (A′, B′ and C′) of the mean.

Solution.

	Results	*Individual Values of* d	d^2
	55.09	0.04	0.0016
	55.14	0.01	0.0001
	55.15	0.02	0.0004
Mean	55.13	Σd 0.07	Σd^2 0.0021

(A) Av. dev. of single determination: $\frac{0.07}{3} = 0.023$ absolute, or

$$0.023 : 55.13 = X : 1000;\ X = 0.42 \text{ part per } 1000.$$

(A′) Av. dev. of arith. mean: $\frac{0.023}{\sqrt{3}} = 0.013$ absolute, or 0.24 part per 1000.

(B) Stand. dev. of single determination: $\sqrt{\frac{0.0021}{2}} = 0.032$ absolute, or 0.58 part per 1000.

(Mean error of single determination)

(B′) Stand. dev. of arith. mean: $\frac{0.032}{\sqrt{3}}$ = 0.018 absolute, or 0.35 part per 1000.
(Mean error of arith. mean)

(C) Probable error of single determination: (0.67)(0.032) = 0.021 absolute, or 0.38 part per 1000.

(C′) Probable error of arith. mean: $\frac{0.021}{\sqrt{3}}$ = 0.012 absolute, or 0.22 part per 1000.

Number of Measurements. The question of how many times an analysis should be carried out in order to have full confidence in its result varies with the nature of the particular analysis. It is customary to run a primary standardization of a solution at least in triplicate; the analysis of an unknown substance usually is done in duplicate or in triplicate depending upon the certainty with which the composition must be known. In very precise work such as an atomic weight determination as many as 10 parallel determinations may be made. Recalling that the accidental error of the mean in a series of measurements varies inversely with the square root of the number of measurements, and bearing in mind that the error usually is small in comparison with the magnitude of the mean itself, we realize that there must come a time when the small, added reliability resulting from still further determinations will not repay the added effort. Let E be the accidental error of the arithmetic mean for n determinations. Then the reliability of the result expressed in terms of the accidental error will vary as follows:

No. of Determinations	*Accidental Error of Arithmetic Mean*
n	E
$2n$	$E/\sqrt{2} = 0.71E$
$3n$	$E/\sqrt{3} = 0.58E$
$4n$	$E/\sqrt{4} = 0.50E$
$5n$	$E/\sqrt{5} = 0.45E$
$10n$	$E/\sqrt{10} = 0.32E$
$100n$	$E/\sqrt{100} = 0.10E$

Obviously it would be a rare occasion indeed when it would be practical to increase the number of determinations a hundredfold if the reliability would be increased only tenfold.

Rejection of a Result. When several parallel determinations have been made, sometimes one result is found to differ considerably from the others. If the analyst is unaware of any reason for the discrepancy, the question arises as to whether or not the suspected result legitimately may be eliminated before computing the mean result. No categorical answer can be given to meet all such cases. However, it can be asserted that there must be a critical value which the suspected result cannot

exceed without the probability of its being a valid member of the series decreasing to the vanishing point. Reliable results will not deviate from the arithmetic mean beyond certain limits. We have seen that large accidental errors are very unlikely and it is extremely improbable that many small inherent errors should all assume the same sign in a given determination. More likely a doubtful value results from a determinate error though the analyst may be unaware of any mistake having been made. A low result in the gravimetric determination of chloride might be due to an unobserved loss of precipitate, for example.

A good many rules have been stated regarding the extent to which a suspected result must deviate from the mean in order to warrant rejection. One rule often followed in quantitative analysis states that if a total of four or more determinations have been made, including the suspected one, the latter may be omitted in computing the mean provided its deviation from the mean of all the others exceeds four times their average deviation. While it may be proved from the theory of probability that one is justified 99.3 per cent of the time if this rule is followed, the rule often allows the inclusion of a result which is likely to be in such error that its inclusion is fully as objectionable as the unjustified exclusion of a result. Therefore, the following rule laid down by Kolthoff and Sandell[2] and based upon the criterion of a number of statisticians seems preferable, namely: *Discard a result if its deviation from the arithmetic mean of the other results exceeds twice the standard deviation of a single measurement.* This rule is valid to an extent of 95.5 per cent; i.e., the odds are 95.5 to 4.5 or 21 to 1 that a result discarded according to this rule is of a determinate nature and not a matter of chance. The rule should be employed only if the number of determinations is at least 4, but not much greater than 10, certainly not greater than 22; in a series of 22 determinations one result will normally show a deviation as great as or greater than twice the standard deviation. Actually in quantitative analysis one usually does not have more than four or five results from which to strike a mean.

It will be recalled (p. 29) that the ratio of the average deviation to the standard deviation of a single measurement is 0.8:1, which is to say the standard deviation is 1/0.8 times the average deviation, or 1.25 times the average deviation. Therefore, the practical application of the above rule to a given doubtful result is that the result is rejected if

$$\frac{\text{Deviation of doubtful result}}{\text{Average deviation of a single measurement}} > 2(1.25) = 2.5$$

and we may thus employ the more quickly obtained average deviation

[2] Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, 1943, p. 276.

instead of the standard deviation in drawing a conclusion regarding the possible rejection of a result.

To illustrate: suppose in an analysis the results obtained in percentages are: 60.64, 60.50, 60.47 and 60.56.

Results	*Deviations*
(60.64), doubtful	(0.13)
60.47	0.04
60.50	0.01
60.56	0.05
Mean 60.51	Mean 0.033

$$\frac{\text{Dev. of doubtful result}}{\text{Av. dev. of single result}} = \frac{0.13}{0.033} = 3.9 > 2.5$$

Therefore reject 60.64

It is worth repeating that no rule, when applied to a finite number of results, is perfect, since the theoretical considerations which form the basis for any such rule rest upon the assumption of an infinite number of measurements. In actual practice therefore we cannot hope to discover and apply a perfect rule for rejecting suspicious results; nevertheless, because it is necessary to deal with a finite (and usually a rather small) number of results, the inclusion of an abnormal result would exercise a disproportionate influence on the mean. The mean result would then be less reliable than if the doubtful one had been rejected. The employment of a practical rule such as stated above is permissible and usually advantageous because of the rather small number of observations practically possible.

Minimizing and Correcting for Errors. It is no more than ordinary common sense for the analyst, when high accuracy is wanted, to use calibrated apparatus and pure reagents and to employ careful technique in the course of an analysis. The custom of running a determination in duplicate or better leads, we have seen, to greater reliability than if a single result is trusted. In addition there are other means of securing greater dependability in the results of our work. Two of these will be taken up.

Running a Blank. A blank is run when it is impossible or impracticable to avoid the introduction of an impurity during the course of an analysis. For example, if the alcohol itself, used as a solvent for the benzoic acid employed as the standard in the titration of a base, contains some acid a blank must be run to determine the acidity of the alcohol. Then a correction for the titration of the base is applied, the magnitude of the correction being obtained through the blank run. If the titration

of a given weight of benzoic acid dissolved in alcohol required 30.00 ml. of base, and a blank run revealed that the acid in the alcohol itself required 0.15 ml. of base, then the benzoic acid obviously was equivalent to only 29.85 ml. of base. In general, a blank run omits the essential substance (the sample; or, in a standardization, the standard itself); all other substances and all quantities and conditions are kept the same as in the analysis proper.

RUNNING A CONTROL. Suppose that there are inherent errors in a given procedure for an analysis. The results of analysis by such a method would always be in error. If, however, a control run is made, the proper correction may be applied to the result. The control consists of a determination in which a known amount of the constituent being sought is analyzed under the same conditions of concentration, temperature, method of analysis, etc., as the unknown. Inasmuch as the result which should be obtained is known in advance, the error may be ascertained by comparison with the actual result of the control analysis. Thereafter, the proper correction on the result obtained for an unknown may be made. It must be kept in mind that here again the value of a control is largely dependent upon "other things being equal"; that is, both qualitatively and quantitatively, the sole difference between the analysis of the unknown and the "analysis" of the control substance should be the use of an unknown on the one hand and that of a known constituent on the other. In order that the control may duplicate the complete situation regarding the unknown it may be necessary to synthesize a control mixture of approximately the same composition that the unknown is believed to have.

SIGNIFICANT FIGURES

In making any observation one and only one uncertain figure should be recorded. (In very exact *calculations* two doubtful figures are carried until the final result is computed; then the result is rounded off to one doubtful digit.) For example, in reading a buret calibrated in tenths of milliliters the reading is made to the hundredths; in observing the swings of the pointer of a balance over its scale which is marked off in units the reading is made to the tenths of a division, etc.

There are good reasons for emphasizing the importance of the proper retention of significant figures. The number of figures employed to express a certain quantity should tell something of the precision involved. When more digits are used than are warranted the implication becomes audacious, since the user gives the impression of exceeding the limitations of refinement of the apparatus from which the observations were taken. When a lesser number of digits than are warranted is employed the analyst is denying himself of his rights; this indicates carelessness on his part or ignorance of his rights.

A number is an expression of quantity. A figure or digit is any of the characters: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9. A *significant* figure is one which indicates the magnitude of the quantity in the place (i.e., the units column, the tenths column, etc.) in which it stands. The number 123 indicates that there are one hundred, two tens and three units, with some doubt as to the exactness of the three units. All of the digits are significant. The zero is employed in two ways, either as a significant figure or only to locate the decimal point. If the magnitude of the quantity in the place where the zero is located is nearer zero than any finite value, then the zero is significant. Thus the zero is significant in the number 1023, for this number states that there are one thousand, two tens, and three units, but no hundreds. Any and all zeros located between two finite digits must always be significant zeros. In the number 0.00123 none of the zeros is significant since they merely locate the decimal point. The location of the decimal point in any measurement is governed by the unit in which the measurement is expressed. Zeros which are not significant may be eliminated, therefore, simply by using a smaller or a larger unit. They also may be avoided by using exponential numbers. Instead of the number 0.00123 meter, the number 1.23 mm. or 1.23×10^{-3} m. may be employed. Instead of the number 15,500 mm., either the number 15.5 m. or 15.5×10^{3} mm. may be used if, indeed, the zeros are not significant. The quantity 15,500 mm. illustrates the cases in which there is no way whatsoever to tell whether or not the zeros are significant. It may be true that the distance between two points is exactly 15,500 mm. in which case the two zeros are significant. On the other hand it may be that the measurement was made with a precision only of ± 1 m.; in that case neither of the zeros is significant. If the measurement actually was made with a precision of ± 1 mm. the quantity should indicate this by being written either 15,500 mm. ± 1 mm., or 15.500 m. Both of these numbers correctly denote that the distance was measured to within a thousandth of a meter (i.e., to within 1 mm.) in accordance with the rule that one and only one uncertain digit—here the second zero—is recorded. In other words the measurement is certainly nearer 15.500 m. than it is to either 14.499 or 15.501 m. To circumvent all ambiguity it is usually best to choose the proper *unit*, that is, a unit which will automatically eliminate zeros which are not significant.

Computations. The following rules should be observed for recording data and for making calculations from these data.

1. As many digits should be used in any observation (i.e., any physical measurement) as will give only one uncertain or doubtful figure. In lengthy and very exact calculations it is desirable to retain, until the final result, two doubtful figures.

2. In rejecting superfluous figures (i.e., in rounding off) increase by 1

the last figure retained if the following rejected figure is 5 or more. If the rejected figure is less than 5 the last figure retained is not altered. It is not necessary to consider at all any digits to the right of that one which is being dropped. For example, 1.235 and 1.2349 rounded off to the hundredths become 1.24 and 1.23, and in the case of 1.2349 the figure 9 need not be considered at all.

3. In addition and subtraction all numbers should be rounded off to an extent corresponding to the first doubtful digit *to the right of the decimal point* in any of the terms. The sum of the terms: 0.0211, 52.18 and 6.05891, assuming the last digit in each case to be uncertain, is

$$\begin{array}{r} 0.02 \\ 52.18 \\ 6.06 \\ \hline 58.26 \end{array}$$

It is useless to extend the digits in any term further than the hundredths column since the second term has its doubtful figure in that column. The first and third terms are made 0.02 and 6.06 to conform to Rule 2. The validity of Rule 3 is obvious if we assume that, had we been able to secure significant figures to the hundred-thousandth place for all three terms, they necessarily would have been respectively between the values given below, for otherwise they would never have been read as 0.0211, 52.18 and 6.05891 as actually they were.

	Smallest possible		*Largest possible*	
1st term	0.02105		0.02114	
2nd term	52.17500		52.18499	
3rd term	6.05891		6.05891	
	58.25496	Rounded off = 58.25	58.26504	Rounded off = 58.27

Therefore, if rounded off in the first place, before adding, we do not offend our precision since the value 58.26 does not differ by more than 1 in the hundredths column as compared with the minimum and maximum of 58.25 and 58.27.

4. In multiplication or division, each factor and the product or quotient may have no greater precision than the least precise term. It must be stressed that here it is the relative and not the absolute uncertainty that is transmitted to the result. It therefore is not always correct simply to round off each factor to the same total number of significant figures as contained in the least precise factor, though often such a rule happens to work. It is safer to proceed as follows: Note the factor having the smallest total number of significant figures and round off all others to the same number of significant figures, unless in so doing a number is

obtained which, ignoring the decimal point, is numerically smaller than the least precise factor; in that case, retain one more significant figure. Suppose we wish the product of (7.765)(5.2)(1.21). The number 5.2 has only two significant figures so that it is the least precise factor. Its true value might actually be 5.1 or 5.3. This number then could be in error by 0.1 in 5.2 or roughly 20 parts per 1000. Therefore, *neither of the other factors nor the final product may exceed this precision.* It is correct to round off the number 7.765 to 7.8, the same number of digits (two) as the governing factor, since 7.8 implies a possible deviation of not more than 0.1 in 7.8 or about 13 parts per 1000, and this is better than the precision of the least precise factor. If, however, the last factor, 1.21, also is cut back to two significant figures and written as 1.2, the precision is less than that of the governing factor, for the number 1.2, with a possible uncertainty of 0.1, might have a deviation of 0.1 part in 1.2 or about 83 parts per 1000. However, if we keep three digits in this factor, using 1.21, its possible deviation is only 0.01 in 1.21 or 8 parts per 1000. Thus the factors and the product should be rounded off as follows:

$$(7.8)(5.2)(1.21) = 49$$

unless the product is to be used in further calculations, in which case it would be written 49.1.

5. Logarithms should be used for multiplication or division except for the simplest operations. Observations usually permit the use of four figures, for with the analytical balance weighings may be made to the ten-thousandth gram and burets are read to the hundredth milliliter; this usually results in a measurement expressed with four significant figures. Although four-place logarithm tables are sufficiently precise for almost all chemical calculations it should be remembered that a five-place table will give an antilogarithm having four digits without interpolation. The use of five-place tables therefore is recommended. Logarithms automatically cause the dropping of the superfluous figures which result in long-hand multiplication. The 10-inch slide rule should not be used in making calculations since it does not yield a high enough precision; however, it may be used as a quick check on computations made with logarithms.

Effect of Errors on Final Result. The reliability of the final result of an analysis evidently depends upon several factors—namely, the errors inherent in the procedure itself, the care with which the work is done and the limitations of the equipment and of the mathematical operations necessary to the calculations. With a proved method of analysis, good equipment and a competent analyst, the precision attained in many analyses should give a deviation of 1 part per 1000 or better. It has already been shown that in the operations of multiplication and division it is the relative precision of the least precise factor which governs the precision of

the final result. If one factor free from error is multiplied by a second factor having an error of 5 parts per 1000 the product also must have an error of 5 parts per 1000. But in subtraction we encounter a situation which may introduce an error the magnitude of which often is not fully appreciated. For example, suppose 1007 is to be subtracted from 1027 and that the last figure in each number is in doubt to the extent of 1. The difference becomes $(1027 \pm 1) - (1007 \pm 1) = 20 \pm 2$. Note that we begin with two numbers each having a deviation of almost exactly 1 part per 1000, but the difference, 20 ± 2, has a possible deviation of 100 parts per 1000! True, in subtraction the errors might cancel, but one cannot be certain of this so that it is necessary to recognize that the result might be in error to the maximum extent. Evidently the best way to hold this type of deviation to a reasonable limit is to arrange things so that the quantity obtained after subtracting is fairly large. If the weight of a precipitate, obtained by subtracting the weight of the empty crucible from that of the crucible plus the precipitate, amounts to about 0.4 g., for example, and if each of the two weighings carries a possible error of 0.2 mg., the weight of the precipitate itself will be known to within 0.4 mg. This represents a deviation of 1 part per 1000 in spite of the subtraction involved. This means that the original sample taken should be of sufficient weight to yield a precipitate of about 0.4 g., which, in turn, means that in the beginning one should make an estimate of just what is a suitable amount of sample.

The number of significant figures employed in reporting the final result depends upon two considerations. If the limitations of the procedure or of the apparatus used are low the result reported cannot imply a high precision no matter how carefully the analysis is carried out. For example, if a sample were weighed on a balance reading only to the third decimal place and amounted to 0.325 ± 0.001 g., the final result of the analysis necessarily would be subject to a possible error of at least 3 parts per 1000 even though perfect checks had been obtained in duplicate determinations. Not more than three figures could be used in reporting the final result (only two if the first digit in the final result were, for example, 9).

On the other hand, if two parallel determinations done with precision apparatus and by a proved method of analysis yield widely divergent results due to poor technique, the reported result again may not indicate a high precision. For instance, if the results were 60.52 and 60.31 there obviously is doubt about the figure in the tenths column, to say nothing of the hundredths column; thus the mean reported result must be 60.4 and not 60.42. However, the tenths column is not doubtful in two such numbers as 60.41 and 60.39 although the digits in the tenths column are themselves different. Simply subtracting the smaller of two duplicate results from the larger will show the place where doubt begins: 60.41

$-$ 60.39 = 00.02. Thus the uncertainty lies wholly in the hundredths column, and it is proper in this case, judging from the individual results alone, to report a mean of 60.40 with the four significant figures.

Questions and Problems

1. Two weighings are made on an analytical balance. If the smaller, 0.2652 g., is subtracted from the larger, 0.2684 g., what is the possible error of the difference in parts per 1000?
   Answer: 63 parts per 1000.
2. In multiplying (8.24) (3.1) (15.29) how should each factor be rounded off and what is the product?
3. In the analysis of a certain sample the following results in per cent were obtained: 10.64 and 10.50. What mean result should be reported, assuming all observations could be to four significant figures? Another analyst obtained for the same substance 10.59 and 10.61. What average should he report?
4. Explain the general conditions of analysis under which a blank should be run; under which a control run should be made.
5. How many significant figures are there in the following numbers? 1.8×10^{-5}; 1001.; 0.050; 0.1001; 16000.
   Answer: 2; 4; 2; 4; (?).
6. In standardizing a sodium hydroxide solution the weights of benzoic acid found to be equivalent to a milliliter of the base in four different titrations were: 0.01224 g., 0.01222 g., 0.01225 g., and 0.01228 g. Calculate the average deviation of a single titration. Should any of the results be rejected?
   Answer: 0.8 part per 1000; 0.01228 is rejected.
7. Five determinations of iron in a sample of ore yielded the values 30.27, 30.29, 30.32, 30.36 and 30.37 per cent iron. Calculate the average deviation, the standard deviation and the probable error of a single determination and of the mean. First decide whether any result should be rejected.
   Answer: Reject none; in order named: 1.1, 1.5, 1.0, 0.5, 0.7 and 0.4 part per 1000.
8. To what decimal place must the samples be weighed in order to have a precision at least as good as 2 parts per 1000 if their weights are respectively about 0.2 g., 2 g., 40 g. and 500 g.?

Chapter 4

THE ANALYTICAL BALANCE. WEIGHING

Mass is the quantity of matter possessed by a body. The weight of a body is the measure of the force of gravity upon the body. Since the force of gravity varies with different localities the weight of a body also varies from place to place; the mass, however, is independent of locality. In spite of the distinction the term weight is often used to imply mass; this is so common that special mention usually must be made of the point if it is desired to emphasize mass in contradistinction to weight.

The Analytical Balance

The analytical balance is the instrument used to weigh a body. The balance, more than any other piece of apparatus, is indispensable to accurate work. It is imperative, therefore, that we know the balance: recognize the essential parts and their functions, appreciate the delicacy of the mechanism and understand how to operate properly this valuable laboratory tool.

Fig. 11 gives a diagram of the ordinary analytical balance. The various parts should quickly come to be recognized and known by their correct names. There is no substitute for an actual demonstration to become familiar with the working parts of the balance. The laboratory instructor may partially dismount the balance in order to show its parts and to explain the necessity of treating the instrument with the respect due any such delicate equipment.

The balance is encased in either wood or metal and has glass windows at the front, back and sides, and usually at the top. The case is mounted upon either three or four legs of which at least two are adjustable in length so that the balance may be properly leveled. A spirit level or sometimes a plumb bob is found inside the case. The base of the balance is of black plate glass and upon it is mounted a heavy column, usually of brass, which supports the beam. A piece of plane agate which is inlaid in the top of the column presents a rust-proof surface to an agate (steel in cheaper balances) knife-edge attached to the center of the beam; it is this contact between the two agates upon which the beam oscillates when the balance is in use.

There are also similar agate-agate contacts between the two stirrups and the extremities of the beam. Thus, as in a fine watch, friction is re-

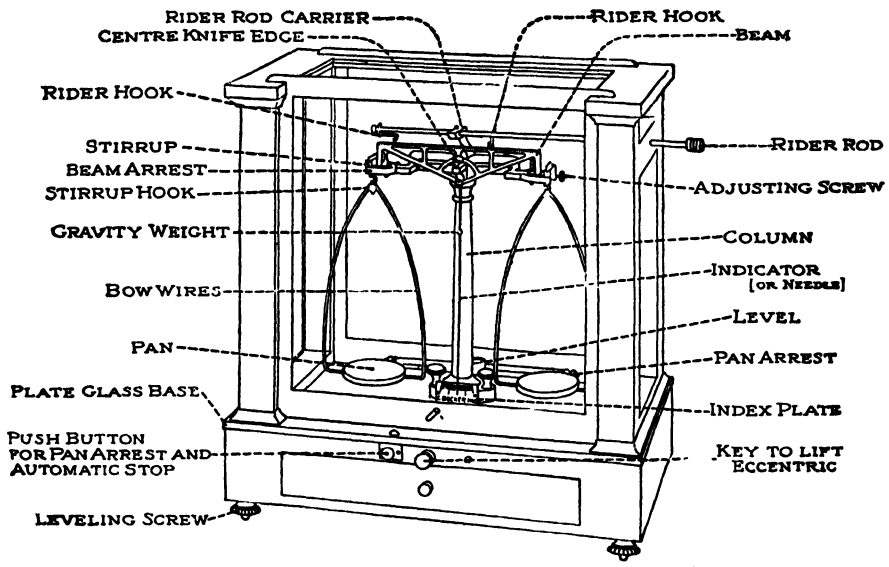


FIG. 11. Essential parts of the analytical balance. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

duced to a minimum by these "jeweled" contacts. The beam itself is graduated either on both sides or only on the right-hand half. The graduations designate milligrams of weight, and there may be either 5, 6, 10 or 12 mg. divisions on the arm. A small wire weight called the rider straddles the beam and indicates according to its location the number of milligrams of weight taken for a given weighing. The position of the rider may be changed by lifting it with the rider hook and horizontally sliding the rider rod.

The balance pans are hung by bow wires from the stirrups. A pointer, also called the indicator or needle, is attached perpendicularly to the center of the beam, and when a weighing is being made it oscillates over a numbered scale in front of the base of the column. A gravity weight, adjustable in height, is fixed upon the pointer; its height regulates the period of oscillation of the pointer and the sensitivity of the balance.

A key or knob located front and center to the case, controls, through the hollow column, the beam support. This support will, when the knob is turned clockwise, lift the beam about a half millimeter, thus breaking the three agate-agate contacts and preventing the danger of chipping the knife-edges if the balance is accidentally jarred while not in use.

Underneath the pans are two pan arrests which push up against the pans with a gentle pressure. They are controlled by the push-button located at the front and near the center of the case. The pan arrests keep

the pans in a plumb position and reduce the likelihood of disturbing the alignment of the beam when anything is being placed upon the pans.

Other Types of Balances

The foregoing discussion deals with the ordinary analytical balance. During the past quarter century various changes have been made in design which facilitate more rapid or more convenient weighing, and in a few instances contribute to a more precise weighing. Such balances may be purchased at somewhat higher cost.

Chainomatic Balances. In this type of balance one end of a small gold chain is attached to the right-hand half of the beam while the other end is attached to a vernier. The vernier may be moved up and down, thus varying the weight suspended from the beam. The vernier gives the reading in grams for the second, third and fourth decimal places and does away with handling of weights except those of hundred-milligram denominations. In some chainomatic balances the use of all fractional weights is eliminated. The sole advantage of these balances is the rapidity of weighing achieved, first, because fractional weights are not handled, and secondly, because the vernier may be elevated or lowered without stopping the swinging of the beam. Fig. 12 shows the characteristic features of chainomatic balances.

Keyboard Balances. Fig. 13 shows a keyboard type of balance. Fractional weights up to one gram are suspended behind the right-hand pan so that they may be attached to or removed from the right stirrup by

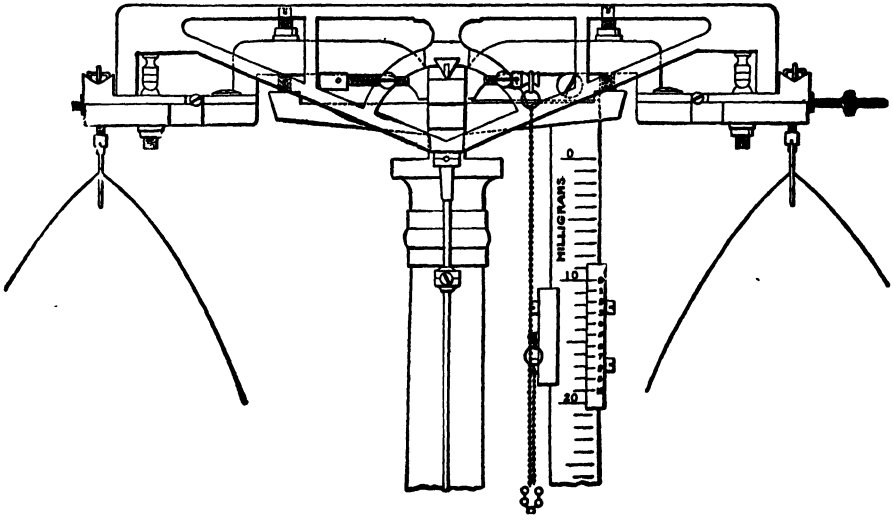


Fig. 12. Details of the chainomatic attachment. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

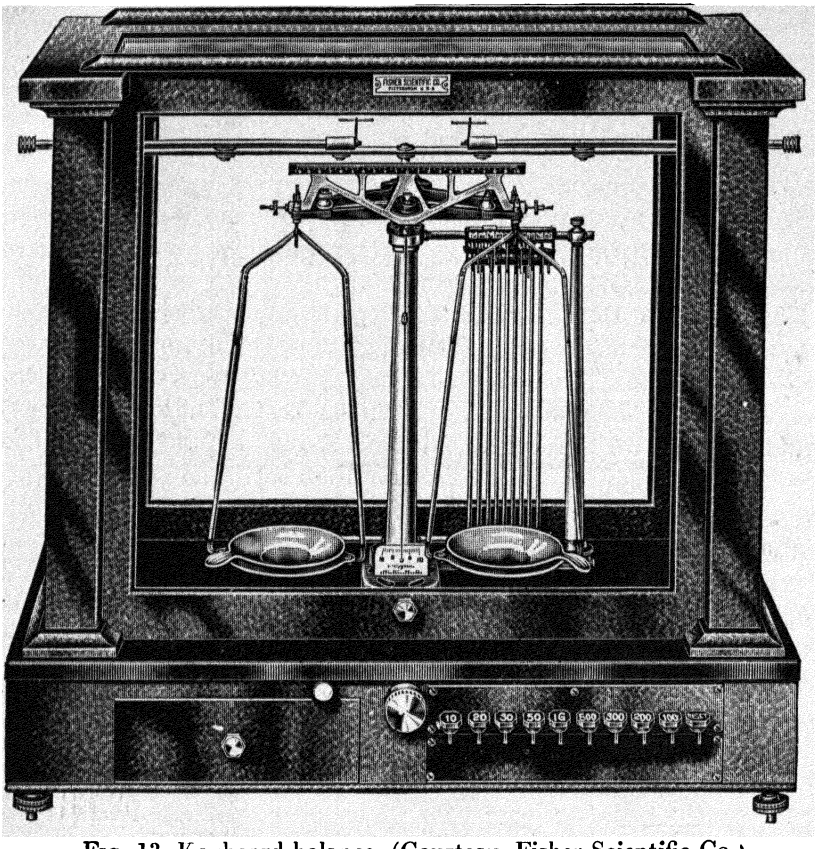


FIG. 13. Keyboard balance. (Courtesy, Fisher Scientific Co.)

operating keys located at the front of the balance case. In a few instruments these mechanical devices have been extended to handle all of the weights. Here too the chief advantage is speed and convenience of weighing.

Damped Balances. Almost any balance may be equipped with a device which causes the pointer to come to rest on the first swing rather than to oscillate back and forth. Such damping is attained by means of oil or air chambers, or by magnetic means, as shown in Figs. 14 and 15. In the latter case an aluminum vane is attached to the end of the beam or is suspended from the stirrup in such a manner that, as the beam swings, the vane moves between the poles of a magnet. Such devices save time in that the position on the scale over which the pointer comes to rest is noted immediately.

Weights. In making a weighing we are simply assembling a combination of masses (weights) equal to that of the object being weighed. A set of weights therefore is required for each balance. Such a set is pictured

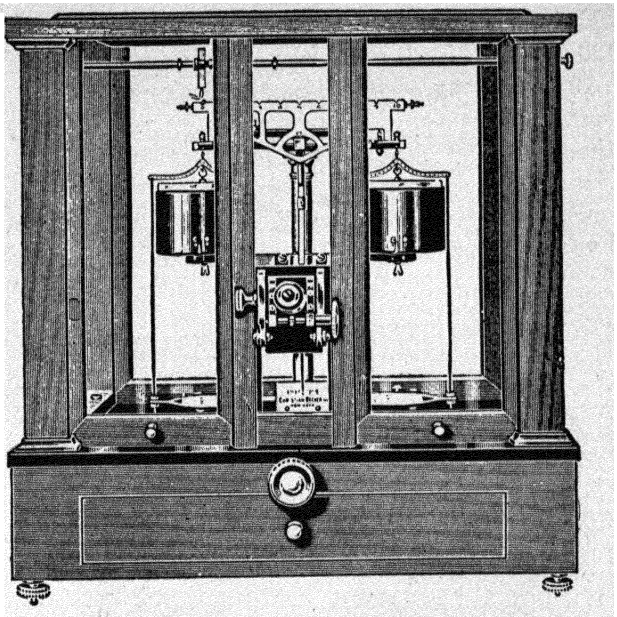


FIG. 14. Air-damped balance. (Courtesy, E. H. Sargent Co.)

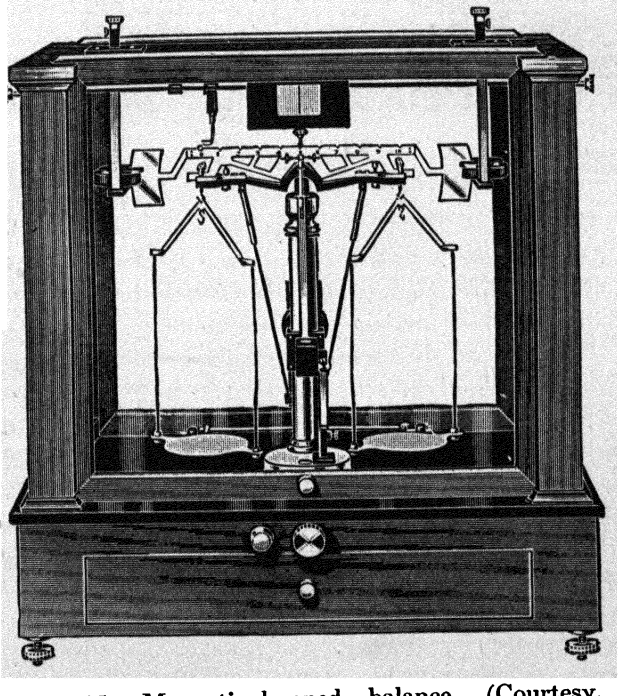


FIG. 15. Magnetic-damped balance. (Courtesy, Christian Becker.)

in Fig. 16. In almost all student sets the following denominations are found: 50, 20, 10′, 10″, 5, 2′, 2″ and 1 g. weights, and 500, 200, 100′, 100″, 50, 20, 10′, 10″ and 5 mg. weights. Smaller weights than the 5 mg. weight are not necessary; in fact no fractional gram weight should be used which is smaller than the greatest number of milligrams which may be had from the rider.

Hardly any given weight is perfect. A weight which, for example, the manufacturer has marked as a 10 g. weight, might in truth be a milli-

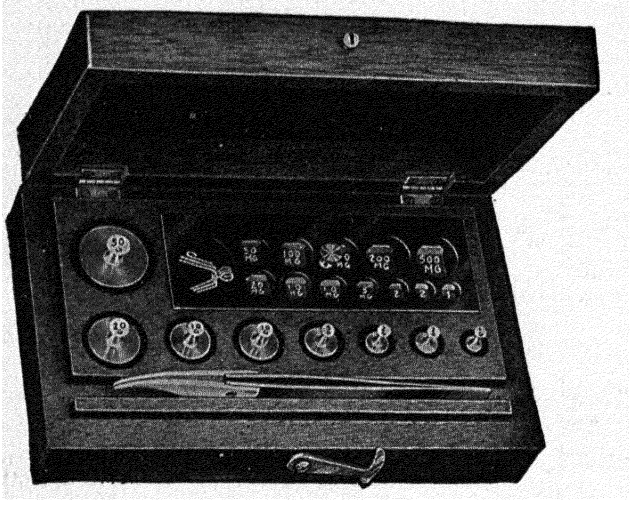


FIG. 16. A set of analytical weights. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

gram or so either greater or less than 10.0000 g. Even if the manufacturer did find that he had made a perfect 10.0000 g. piece, as checked on his balance, this same weight on another balance might not act as a perfect ten. This is due, chiefly, to the fact that in spite of the best efforts of the manufacturer the arms of the balance may be slightly unequal in length, giving slightly different beam leverages to the right and left of the fulcrum. It is necessary then, for really accurate weighing, to check each piece in the box of weights against a standard weight and, once this has been done, always to use these same weights with a given balance. The calibration of weights will be taken up in a later section.

Two classes of weights may be purchased: Class S weights for weighings in ordinary analyses, and Class M weights for work of high accuracy. Once calibrated, however, either class is entirely satisfactory. Table 1 lists the tolerances recommended by the U.S. Bureau of Standards.

Table 1

U.S. BUREAU OF STANDARDS TOLERANCES FOR CLASS S WEIGHTS

Weight in g.	*Tolerance in mg. (either + or −)*
100	0.5
50	0 3
20	0 2
10	0.15
5	0.15
2	0.10
1	0.10
0.5	0.05
0.2	0.05
0.1	0.05
0.05	0.03
0.02	0.03
0 01	0.02
0 005	0.02

WEIGHING

Before taking up different methods of weighing, the following points should be studied carefully until so familiar that they become second nature to the analyst.

1. Always use the same balance throughout a given analysis. If the balance is shared by two or more persons, coöperate with the others in keeping the balance in perfect order.

2. The balance must be mounted so that it is free from vibration. In laboratories in which brick walls of the balance room extend through floors continuously to the earth the balance may be placed upon a shelf attached to the wall (the shelf must never rest upon the floor); otherwise a pier resting upon the ground should be employed.

3. The balance must never be subjected to direct sunlight or to drafts. It is best to keep the windows of the room closed and the shades drawn. The room should be well lighted with several lights so that no shadows are cast.

4. Avoid the habit of comfortably placing the elbow alongside the balance with the hand against the side of the balance. This heats up one side of the balance and makes accurate weighings impossible.

5. Never weigh an object which is warm. Wait until it has reached room temperature. A hot object produces an upward motion of the air around the object and this causes low results in weighing.

6. Except when weighing an object which cannot possibly injure the

pan, never place the substance directly upon the pan; instead place it in a container: a watch glass, crucible, etc. It is unnecessary to place any desiccant within the balance case.[1]

7. Usually the first step in a weighing is to obtain the equilibrium point (also called the rest point and, if the pans are empty, the zero point), that is, the position over the scale at which the pointer freely rests. If the equilibrium point is more than one scale division from the center of the scale, request the instructor to readjust it. This he may do by varying the mass on one side of the beam through the adjusting screw.

8. When the beam is released bring the agate knife-edges into contact with their planes very carefully; abrupt lowering of the beam might result in chipping the agate prism. Put the beam in motion by momentarily dropping the rider at any point on the beam. This is better than wafting a current of air toward the pan with the hand, which sometimes results in accidentally hitting the pan and also may blow away any powdered substance being weighed.

9. During a weighing, when it is desired to stop the oscillation of the pointer, do so by releasing the pan arrests at the instant the pointer crosses the mid-point of the scale. This prevents jarring. Then carefully raise the beam support. In putting weights on the pan or removing them be sure that the beam is locked.

10. Weights should be handled only with the forceps. Weights are always placed on the right-hand pan. Large weights should be placed near the center of the pan, for otherwise the pan will not hang in a plumb position when the arrests are lowered. Place fractional weights on the pan in order of their denominations. In handling large weights hold the forceps with the concave edge up. With fractional weights hold the concave edge down and pick up the weights with the points of the forceps.

11. Keep the fractional weights in the box in a definite sequence (see Fig. 16). It will save time if the turned-up edges are arranged consistently, e.g., always at the top of their compartments.

12. In recording the sum of the weights in the notebook first list the weights which are missing from the box. Then check the list as the weights are removed from the pan. The checking requires only a moment of time; one error in summing up the weights may cost days or even a week in repeating an experiment.

13. When a weighing has been completed see that everything is left in good order: the beam support and pan arrests are up; the rider is on its hook and the rod has been pushed back into the case; the base of the balance and the pans are brushed clean; the window is closed; the chair has not been left out on the floor where someone may trip over it.

Equilibrium Point. The equilibrium point or rest point (the zero point if the pans are empty) of the balance is that position of the pointer

[1] Kuhn, *Chem. Ztg.*, **34**, 1097 (1910).

on the scale at which it eventually would come to rest after being set into motion. It is not necessary to wait until the pointer actually comes to a standstill. Rather, if the points to which it successively swings to one side and the other are noted the arithmetic mean will give the equilibrium point, provided only that an odd number of readings are taken on one side and an even number on the other side. Due to friction within the balance, and to air resistance, the oscillations gradually become of smaller and smaller amplitude, and each swing accordingly will become slightly shorter than the preceding one. Thus the final position of the pointer will not be midway between the extremities of two successive swings, nor even midway between the average of two successive positions on the right and two on the left. The equilibrium point will be, however, that

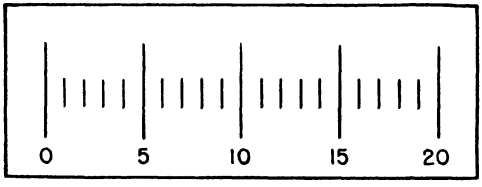


FIG. 17. The scale of an analytical balance.

position halfway between the average of n points on one side and $n + 1$ on the other, successively taken.

Suppose, as a simple example, a balance is so adjusted that the equilibrium point is actually 10.0, the scale being numbered as seen in Fig. 17. (This does away with negative values which result if the middle of the scale is numbered zero.) Suppose further that the slow-down amounts to one scale division for each half oscillation. (As a matter of fact the decrease is seldom this great.) If the first reading were at 3.0 the succeeding readings would be as follows:

Left	*Right*
1st reading 3.0	1st reading 16.0
2nd reading 5.0	2nd reading 14.0
3rd reading 7.0	3rd reading 12.0

If we took the first two readings both right and left we would have averages of 4.0 on the left and 15.0 on the right. The mean of 4.0 and 15.0 is 9.5, which differs by 0.5 from the equilibrium point of 10.0 assumed in our example. Similarly using all three values on both sides gives 9.5. However, if the first two readings on the left and the first alone on the right, or if all three on the left and the first two on the right, are used, the average of 10.0 is obtained; we repeat, then, that an odd number of readings must be taken on one side and an even number on the other, and all must be taken successively.

To determine the equilibrium point proceed as follows. Brush off the pans with a camel's-hair brush, then close the window and lower the beam support and the pan arrests. Drop the rider momentarily on the beam, remove the rider, and allow one or two oscillations to take place. An amplitude of about 8 to 12 divisions is suitable. Then record the readings of the pointer, twice on one side and three times on the other. Since the scale is marked off in units readings are taken to the tenths, for this gives one doubtful digit. To illustrate:

Left		*Right*	
1st reading	5.1	1st reading	15.0
2nd reading	5.3	2nd reading	14.8
3rd reading	5.5	Average	14.9
Average	5.3		5.3
		2	20.2
		Equilibrium point	10.1

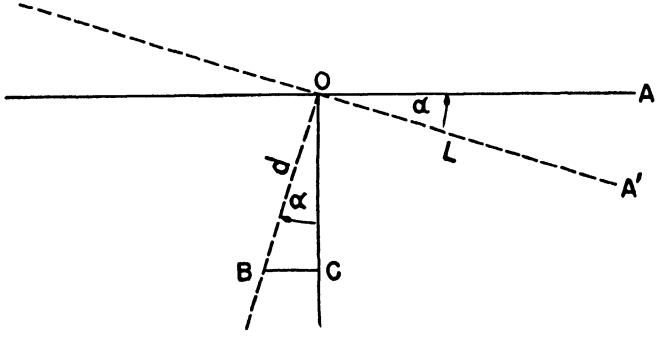


FIG. 18. Factors influencing the sensitivity of a balance.

SENSITIVITY OF THE BALANCE

The sensitivity of the balance is defined as the number of scale divisions by which the equilibrium point of the balance shifts due to an excess of one unit of weight, usually taken as 1 mg., on one of the pans.[2]

Why should different balances have different sensitivities, and why should the sensitivity of a given balance, instead of being a constant, change with different loads? The answers to these questions are found in the laws governing simple levers. A lever is in a condition of equilibrium when the force of moments which tend to impart a clockwise rotation equals that tending to give a counterclockwise rotation. In Fig. 18 let the

[2] Sensitivity is sometimes defined in other ways. Manufacturers refer to the sensitivity as the smallest mass which produces an observable shift of the equilibrium point. The term also occasionally is used to denote the number of tenths of milligrams which will cause a shift of the equilibrium point amounting to one scale division.

solid lines represent the equilibrium position of the balance with no load and the dotted lines the equilibrium position after the excess weight, m, has been added to the right-hand pan. Two opposing forces are at play: the force tending to cause a clockwise rotation produced by the effect of gravity, g, on the excess weight, and the force tending to cause the counter-clockwise rotation produced by the effect of gravity on the mass of the beam, M, acting through its center of gravity, B, which is located at a distance, d, from the fulcrum, O.

The effect of a force in turning a body about any axis is called the "moment" of the force about that axis; it is calculated as the product of the force (acceleration of gravity, g, multiplied by the mass) and the perpendicular distance from the axis to the line of action of the force. Therefore

$$\text{(1)} \qquad Mg.BC = mg.OA$$

Now angle BOC is equal to angle AOA′ since the corresponding sides of the two triangles are mutually perpendicular. Call these angles α. Furthermore, line OB $= d$ and OA′ $=$ L, the arm of the beam. Thus

$$BC = d \sin \alpha$$

and

$$OA = L \cos \alpha$$

Substituting these values in equation (1) yields

$$Mgd \sin \alpha = mgL \cos \alpha$$

or (2)

$$\frac{\sin \alpha}{\cos \alpha} = \tan \alpha = \frac{mL}{Md}$$

With the balance we are concerned only with small angles in which case the tangent is practically equal to the angle itself (in radians). It follows therefore that the sensitivity of the balance, S, i.e., the displacement or shift made by the pointer,

$$\text{(3)} \qquad S \cong \frac{\alpha}{m} = \frac{L}{Md}$$

From equation (3) it is seen that the angular displacement, and thus the sensitivity, increases as the length of the beam increases. It decreases as the mass of the beam increases; thus the beam and the supported pans should be of light construction, but rigidity of the beam should not be sacrificed. The sensitivity also decreases as the distance from the center of gravity becomes greater. Therefore the sensitivity may be increased by raising the center of gravity of the balance (by elevating the gravity bob; see Fig. 11). The center of gravity, however, can never be above the knife-edges, since then the balance would be in unstable equilibrium and could not oscillate. With a higher center of gravity and greater sensitivity

the period of oscillation becomes greater, and since the latter extends the time necessary to make a weighing, a compromise between higher sensitivity and shorter period must be made.

The assumption has been made that the three knife-edges of the balance are in the same plane. However, with heavier loads on the balance the beam will bend slightly, with the result that the knife-edges at the terminals are below the one at the fulcrum; this may bring about a rapid falling off of the sensitivity with increasing loads. In fact some balances which are to be used regularly for rather heavy loads are constructed purposely with the extreme knife-edges slightly higher than that at the center, so that under loads the three come more nearly within the same plane.

Determination of Sensitivity

As will be explained later, for accurate weighings the figure for the fourth decimal place is established by use of the sensitivity of the balance. The sensitivity at various loads therefore must be determined. To do so proceed as follows: Determine the equilibrium point with the pans empty as already explained. Do this in duplicate. The duplicate runs should check within 0.2 of a scale division. Suppose the mean result is 9.8, that is, two-tenths of a scale division to the left of the center-point. Now place the rider momentarily at any point on the beam so that the pointer begins to swing with a moderate amplitude. Then place the rider exactly on the 1 mg. mark on the beam. The balance now operates with one more milligram of weight on the right side than on the left; the equilibrium point therefore must shift to the left and the number of scale divisions by which it does shift will, by definition, be the sensitivity of the balance for a zero load. Determine this new equilibrium point in duplicate, again being sure that these duplicate results check within 0.2 scale division. Suppose the mean result is 6.5. The difference between this and the original equilibrium point (before adding the 1 mg. excess weight) is $9.8 - 6.5 = 3.3$. This then is the sensitivity of the balance for a zero load. Let us repeat that this simply means that when the two pans are in a state of imbalance to the extent of exactly 1 mg., the equilibrium point shifts by 3.3 scale divisions. Conversely, if later, in making a weighing with this balance, we found that the final equilibrium point differed from the original equilibrium point by 3.3 scale divisions, the object being weighed would differ in weight from the sum of weights being used by 1 mg.

Next determine the sensitivity of the balance for a 10 g. load. To do this, place a 10 g. weight on each of the pans (the rider is not on the beam, of course) and determine the equilibrium point, again in duplicate. Do not be disturbed if this equilibrium point is not the same as was obtained with both pans empty. Remember that the beam may be slightly bent under

the 10 g. load, that friction will be greater under the heavier load, and, furthermore, that few weights are perfect so that the two 10 g. pieces may, in fact, be of not quite the same mass. For any of these reasons the equilibrium point now may not be at 9.8. Say that it proves to be 10.1. Next, after setting the pointer to swinging, place the rider at 1 mg. and determine again the equilibrium point. If this were, say, 7.0, the sensitivity for the 10 g. load obviously would be 10.1 − 7.0 = 3.1. In like manner determine the sensitivity for a 20 g., 30 g., 40 g., and 50 g. load, and then make a graph of the results, plotting the sensitivity as the ordinate and the load in grams as the abscissa. Place the graph, which will be similar to

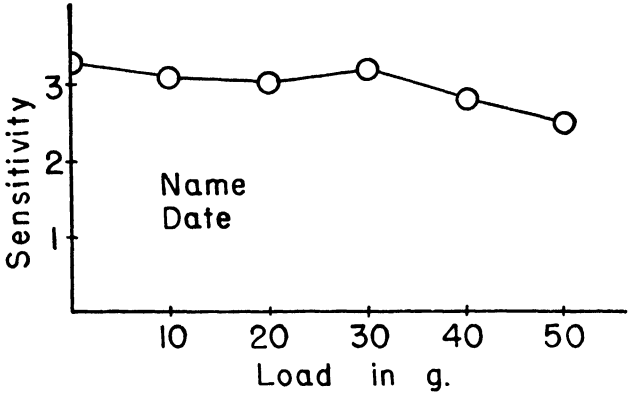


FIG. 19. Sensitivity curve of a balance.

Fig. 19, in the upper left-hand corner of the balance window. It should be mentioned that a balance should not be subjected to a load for which the sensitivity is less than 40 per cent of the maximum sensitivity.

It sometimes happens in determining the sensitivity of the balance, especially for heavier loads, that the sum of the (imperfect) weights on one pan differs from the sum on the other pan (even though the same denominations are placed in both pans) to such an extent that the pointer swings entirely off the scale. If this happens place the rider at such a position on the beam that the initial equilibrium point for the load is near 10. After determining the equilibrium point in duplicate move the location of the rider by exactly 1 mg. and determine the new equilibrium point in duplicate. This will give the sensitivity even though the rider was used twice for the given load, for here also the shift in equilibrium point was caused by a difference in weights of 1 mg. by the rider.

METHODS OF WEIGHING

Direct Weighing. Method of Swings. The object to be weighed always is placed on the left-hand pan. Due to inequality in the lengths of

the arms of the balance, weighings made by direct methods do not represent the true masses of the objects but are proportional to them; thus they give a correct ratio of masses. This method of weighing is reliable when results are sought on a percentage basis, since any difference in the lengths of the two arms is compensated. (If the absolute or true value of the mass is wanted the weighing may be carried out by the direct method and the weight obtained multiplied by the arm ratio, p. 54, or else either the Gauss method, p. 54, or the Borda method, p. 55, of weighing may be employed.)

Procedure. First determine the equilibrium point of the balance. Then place the object on the left-hand pan. Next with the forceps place on the right-hand pan that integral weight judged to be nearest the mass of the object. Lower the beam support just enough to reveal in which direction the pointer moves. If the weight chosen is too heavy, lock the beam support and substitute the next lighter weight. If this weight is not too heavy it is left on the pan and the next weight in descending order is added, and the beam support again is lowered to show the inequality. If the total weight at this point is too great the last piece added is replaced with the one just lighter than it; if the total weight is not too heavy the last weight which was added is left on the pan and, in addition, the next lower weight is placed on the pan. This process is continued with smaller and smaller integral weights until finally the 1 g. weight is either used or rejected. Then the beam support is kept lowered as the fractional gram weights are tried, since the pan arrests are strong enough to hold the pointer midway on the scale when the state of imbalance is less than a gram. The fractional weights are added in the same systematic fashion as were the integral weights starting with the 500 mg. piece. The state of imbalance may be tested by lowering the pan arrests just enough to show which direction the pointer takes. In the above manner the total number of separate pieces used will automatically be the smallest number possible. When two different pieces of a given denomination are available always use the one-dot piece in preference to the two-dot weight. (See p. 57.)

The rider is now placed upon the beam and adjusted so as to cause the same equilibrium point as was found at the beginning with no load. By this method the rider most likely will not be situated finally at a whole milligram division on the beam, and, whether this is so or not, the last two digits—i.e., for the third and fourth decimal places—are read directly from the beam.

The figure for the fourth decimal place is more quickly established in the following manner: Instead of placing the rider at such a point on the beam as will regain the original equilibrium point, simply locate it on that whole milligram division on the beam which is most nearly correct to balance the object being weighed. Then determine in duplicate the equilibrium point. The difference between this equilibrium point and that for empty pans is divided by the sensitivity of the balance (for the par-

ticular load; consult the sensitivity curve). The quotient gives the degree of imbalance in terms of milligrams, and this must be added to or subtracted from the sum of the weights on the right pan, including the rider. The following example should make the method clear.

(a)	Equilibrium point, zero load	9.8
(b)	Equilibrium point with weights totaling 9.87 on pan, and rider at 6.0 on the beam	10.9
(c)	Shift of equilibrium point	1.1 scale divisions
(d)	Sensitivity of balance for 10 g. load	3.1
(e)	State of imbalance = 1.1/3.1 =	0.3 mg.

The total weight therefore is recorded as 9.876 g. + 0.3 mg. = 9.8763 g. This is still not the weight accepted by the analyst, however, since the *weights correction* (see Table 3, p. 61) has not yet been applied. Note that this sensitivity correction of 0.3 mg. is added since the equilibrium point with the load was greater than that with pans empty, meaning, of course, that the 9.876 g. was too light for the object. When the equilibrium point with the load is smaller than that with pans empty the sensitivity correction is subtracted from the total weights on the pan. It hardly needs to be mentioned that to attain a precision of a tenth milligram the sensitivity of the balance must be 2.0 or greater since a weighing involves taking two equilibrium points both subject to an error of 0.1 scale division.

Direct Weighing by Single Deflection Method. A more rapid procedure known as the single deflection method[3] is often employed. It is not recommended when weighings of the highest accuracy are desired[4] nor when hygroscopic substances are weighed. By the adjustment screw of the beam the left arm of the balance is made permanently heavier than the other so that when the pointer is free to swing, a definite deflection results due to the added moment on the left arm. The deflection should amount to about five or six scale divisions, i.e., to about 15 or 16 on the scale. In weighing an object it is placed on the left pan as usual and weights are placed on the right pan, and the rider located so as to give the same single deflection as with pans empty. Or, provided a sensitivity curve has been constructed also using the single deflection method, the duplication of the original equilibrium point is unnecessary; rather, the fourth decimal place is calculated from the two equilibrium points and the sensitivity as usual.

The only advantage of this method of weighing is its speed. Its use requires a balance with separate beam and pan releases and the latter must be carefully adjusted so that it gives no impetus to the pans when

[3] Britton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).
[4] Lin, *J. Chem. Education*, **16**, 340 (1939).

released. If the single deflection method is to be used the beginner should practice releasing the pans until a constant deflection can be obtained at will.

Method of Double Weighing (Gauss). For very accurate work this method, proposed by Gauss, is often employed. It eliminates errors otherwise resulting from inequality in length of balance arms, and the results give about twice the accuracy obtained by other methods. The object is weighed first on one pan and then on the other. The mean of the two results is taken as a measure of the true weight.

It follows from the principle of the lever that if an object of true mass, M, is placed upon the left-hand pan and is counterbalanced by weights, W_r, on the right-hand pan,

$$ML_l = W_rL_r \tag{4}$$

where L_l and L_r are the lengths of the left and right arms of the balance, respectively. Placing the object now on the right-hand pan and counterbalancing with weights W_l on the left-hand pan, we have

$$ML_r = W_lL_l \tag{5}$$

The product of equations (4) and (5) yields

$$M^2 = W_lW_r$$

from which

$$M = \sqrt{W_lW_r}$$

Usually the values W_l and W_r are nearly equal and as a close approximation

$$M = \frac{W_l + W_r}{2} \tag{6}$$

M, determined by this method, gives the true mass of the object.

Ratio of Lengths of Balance Arms. Equations (4) and (5) above may be combined and used to calculate the ratio of the arms of the balance. Dividing (4) by (5) yields

$$\frac{L_l}{L_r} = \sqrt{\frac{W_r}{W_l}} \tag{7}$$

In a good balance the arms will seldom differ in length by more than 1 part in 50,000. It must be realized that the ratio L_l/L_r is not a constant even for a given balance but is a variable dependent upon conditions. If one arm is at a slightly higher temperature than the other the ratio would be changed. Under different loads the ratio may be different. It follows that the ratio of arm lengths as determined under one set of

conditions must not be used for the calculation of the true mass of an object when weighed under different conditions.

Weighing by Substitution (Borda). This is a second method used for finding the true mass of an object regardless of the fact that the balance arms may be of slightly different lengths. The object of mass, M, is placed on one pan, say the left-hand pan, and counterbalanced by another body (e.g., copper shot) of weight T, called a tare. The equilibrium point is then determined. The object is next removed from the pan and replaced by calibrated weights (see p. 57) of such mass, W, as to give the same equilibrium point. From the first counterbalancing we have

$$ML_l = TL_r \tag{8}$$

and from the second

$$WL_l = TL_r \tag{9}$$

Therefore $ML_l = WL_l$

or $M = W$

This is to say, ignoring the buoyancy effect of the air which will be discussed below, the mass of the object is equal to that of the weights; this must be true since both objects and weights have been acting through the leverage of the same arm, L_l.

Whenever highest accuracy is essential, one of the methods for obtaining true weights must be employed. For example, in the calibration of weights and of volumetric apparatus (p. 57 and Chapter 5) the substitution method has been recommended.

Buoyancy Correction in Weighing. It will be recalled that Archimedes' Principle states that when a body is completely immersed in a fluid, liquid or gaseous, its weight is diminished by an amount equal to the weight of the fluid displaced. When a weighing is made in air both the object and the weights are subject to the buoyancy effect of the surrounding air. The denser the body is, the less air it will displace per unit of mass. The weight of an object in air is the result of the downward pull of gravity and the upward buoyant effect of the air upon both object and weights. The net effect of the latter force will depend upon which displaces more air, the object or the weights; since the object weighed is almost always less dense than the weights themselves it follows that the weight of the object in air usually will be less than its weight *in vacuo*. The buoyancy effect will be zero only in the rare instance when the object and the weights displace the same amount of air, that is, when their densities are equal. Because it is impracticable to carry out a weighing in a vacuum, a correction for buoyancy always must be made in very exact work. As a rule the correction is ignored for weighings in quantitative analysis, first

because the air displaced by the object is small and also because there is generally a canceling out of the effect due to the fact that the calculations so often are based upon two weighings (the sample and the precipitate, for example) involving substances of not widely differing densities. If, however, large volumes of air are displaced by the object, as in the calibration of volumetric apparatus, or in the weighing of gases and in density determinations, the buoyancy effect must be taken into account.

The weight *in vacuo* may be calculated as follows. It is obvious that the weight *in vacuo*, W_v, is the weight in air, W_a, plus the buoyancy effect on the object, minus the buoyancy effect on the weights, or

(10) $W_v = W_a +$ (Buoyancy Effect, Object) $-$ (Buoyancy Effect, Weights)

Now the buoyancy effect on the object is the product of the volume of the air displaced by the object (equal to the volume of the object itself) and the density of the air. Thus the first term within the parentheses of equation (10) becomes $\frac{W_v}{D_o} \cdot D_a$, where W_v is the *in vacuo* weight of the object, D_a and D_o are respectively the densities of air and of the object in g. per ml. Similarly the second term in the parentheses becomes $\frac{W_v}{D_w} \cdot D_a$, where W_v is the *in vacuo* value of the weights employed and D_w is the density of the weights. Thus equation (10) becomes

(11) $$W_v = W_a + \frac{W_v D_a}{D_o} - \frac{W_v D_a}{D_w}$$

In general W_v and W_a do not greatly differ, so that equation (11) may be written

$$W_v \cong W_a + \frac{W_a D_a}{D_o} - \frac{W_a D_a}{D_w}$$

or

$$W_v \cong W_a \left(1 + \frac{D_a}{D_o} - \frac{D_a}{D_w}\right)$$

from which

(12) $$W_v \cong W_a \left[1 + D_a \left(\frac{1}{D_o} - \frac{1}{D_w}\right)\right]$$

The density of air varies with the temperature, the barometric pressure and the humidity. In the laboratory the air is usually moist and between temperatures of 15° and 30° and pressures of 720 mm. and 780 mm. A milliliter of dry air at 15° and 780 mm. weighs 0.00126 g., whereas a milliliter of air saturated with water vapor at 30° and 720 mm. weighs 0.00108 g. As an average between these extremes we may employ a density for moist air of

0.0012 and use this value in equation (12). Doing this, and substituting a value of 8.4 as the density of brass, for D_w, we have

$$W_v \cong W_a \left[1 + 0.0012 \left(\frac{1}{D_o} - \frac{1}{8.4}\right)\right] \tag{13}$$

for calculating the true, *in vacuo*, weight of objects weighed in air with brass weights at ordinary room conditions.

Calibration of Weights[5]

It already has been pointed out that the weights in any set are not likely to have exactly the mass that their nominal values indicate, and therefore should be calibrated. For the ordinary weighings of quantitative analysis it is not necessary that we know the absolute values of the weights. It is essential, however, that the various weights of a given set agree among themselves; i.e., either the 50 mg. weight must be exactly 5 times as heavy as the 10 mg. weight or else we must know to what extent it varies from 5 times the 10 mg. weight; either the 2 g. weight must be exactly 200 times as heavy as the 10 mg. weight or else we must know to what extent it departs from 200 times the 10 mg. weight, and so on. The calibration of the weights consists of the determination of such deviations. The calibration may be relative, in which case we determine the values of the several denominations based upon one single weight of the set; or it may be absolute, in which case the value of each weight in the set is based upon a single certified weight the absolute value of which has been established by the U.S. Bureau of Standards.

Before beginning a calibration the weights should be wiped clean with a piece of Kleenex tissue. If the set contains more than one piece of a given denomination, e.g., two 100 mg. weights, the duplicates should be given distinguishing marks. Usually they are marked with one and two dots by the instructor. We shall designate such duplicates as 100′, 100″, etc. An auxiliary set of cheap weights must be available to be used as tares.

The principle of a calibration is as follows. Either the 5 mg. weight (for balances having a beam divided into less than 10 mg. divisions) or the 10′ mg. weight (for balances having a 10 mg. beam) is arbitrarily assigned a weight of 5.00 (or 10.00) units. The unit is approximately, but only by coincidence exactly, 1 mg. Suppose we are working with a balance with a 10 mg. rider; i.e., there are 10 divisions on the beam. First, by the substitution method, the rider is compared with the

[5] Richards, *J. Am. Chem. Soc.*, **22**, 144 (1900); Semon, *J. Chem. Education*, **2**, 132 (1925); Hurley, *Ind. Eng. Chem., Anal. Ed.*, **9**, 239 (1937); Thornton, *J. Chem. Education*, **14**, 270 (1937); Blade, *Ind. Eng. Chem., Anal. Ed.*, **11**, 499 (1939).

10′ mg. weight; then the 10″ mg. weight is compared with the 10′ mg. weight; the 20 mg. weight is compared with the 10′ mg. plus the 10″ mg. pieces, and so on through all the fractional weights and the integral weights. These comparisons yield the values for each piece in relative terms, of course, based upon our arbitrarily assigned unit. As we proceed to whole-gram weights the comparative value for a given weight differs rather widely from the nominal value of the weight. Accordingly, it is customary, once all the relative values are obtained, to assign an exact value to one of the larger weights, usually 10.0000 g. to the 10 g. weight. It then becomes the new (arbitrary) standard in terms of which all of the other pieces are expressed. Finally, if a certified weight is at hand, say a 10 g. unit checked by the Bureau of Standards, the absolute values of all the weights of the set may be computed.

Procedure. First calibrate the rider. Place the rider exactly on the 10 mg. division; put an auxiliary 10 mg. weight on the left-hand pan as a tare and determine the equilibrium point in duplicate, calculations being made to the hundredths. Remove the rider from the beam, place the 10′ mg. weight on the right-hand pan and again determine the equilibrium point. To illustrate the calculation involved, assume the two equilibrium points were 9.84 and 9.67 respectively, and that the sensitivity of the balance was 2.8. Then $\frac{9.84 - 9.67}{2.8} = 0.06$, which is the amount by which the 10′ mg. weight and the rider differ. Since the second equilibrium point is smaller than the first it is obvious that the rider is lighter than the 10′ mg. weight, and since we assigned a value of 10.00 units to the 10′ mg. weight the rider must weigh 9.94 units.

Now compare the 10″ mg. weight with the 10′ mg. weight in the same general manner. Suppose it is found to be 0.08 unit lighter than the standard 10′ mg. weight; it then would have a value of 9.92 units. Next calibrate the 20 mg. weight. To do this, place the two 10 mg. weights on the right-hand pan and a 20 mg. auxiliary weight on the left-hand pan. Determine the equilibrium point. Remove the two 10 mg. weights from the right-hand pan, replace with the 20 mg. weight from the analytical set and determine the new equilibrium point. Again, just as before, calculate the number of units by which the 20 mg. weight from the analytical set is heavier or lighter than the sum of the two 10 mg. weights of the set. Say the 20 mg. weight is 0.06 unit heavier than the sum of the two tens. Then the 20 mg. weight must have a value of $(10.00 + 9.92) + 0.06 = 19.98$ units.

The value of the 50 mg. weight is next determined in terms of the 20 mg. plus the two 10 mg. weights plus the rider placed at the 10 mg. division of the beam, again, of course, by substitution, using an auxiliary 50 mg. weight as a tare. In the same manner comparisons are made for

each denomination of the whole analytical set, both fractional and integral weights. When this is completed, data such as that given in the first five columns of Table 2 may be assembled.

All of the figures of the table through Column 5 are based upon the assignment of 10.00 units to the 10′ mg. weight. The choice of such a small weight as the standard is advantageous in that one unit is just about 1 mg., but this would result in rather large corrections as we come to the larger denominations (see Column 5). We may circumvent this inconvenience by assigning a new, heavier standard and reëvaluating all denominations on the new basis. For example the 10′ g. weight may now be assumed exactly equal to 10.0000 g. Upon this basis, since we have established the relative value of the 10′ g. weight as 9941.20 units (see Table 2),

$$9941.20 \text{ units} = 10.00000 \text{ g.}$$

$$\text{Therefore} \qquad 1 \text{ unit} = \frac{10.00000}{9941.20} \text{ g.} = 1.005905 \times 10^{-3} \text{ g.}$$

If then we multiply each unit value of Column 5 by this value of one unit, 1.005905×10^{-3} g., we shall have the relative value of each denomination in terms of grams. The same thing may be accomplished, with less labor, in the following manner: Calculate the aliquot part of 9941.20 for each weight by multiplying by that part of 10 which the denomination represents. That is to say, for the 2 g. weight, multiply 9941.20 by 0.2; for the 50 g. weight multiply 9941.20 by 5, etc. Place these aliquot parts in Column 6. If a given number in Column 5 is identical with the corresponding number in Column 6 then, and only then, that piece is a perfect weight (as based upon our arbitrary assignment). If a number in Column 5 is smaller (or larger) than the corresponding number in Column 6 then that piece is not a perfect weight but is lighter (or heavier) by an amount represented by the difference in the two columns. Column 5 minus Column 6 thus gives the correction, in milligrams, which must be applied to the denominational value of each weight in order to have its correct value, based on the assumption that the 10′ g. weight is perfect. Place these corrections in Column 7 and then obtain Column 8 by algebraically adding the correction to the figures stamped on each piece. In Column 8, therefore, the true, *relative* value of each weight is found.

It might be repeated for emphasis that in most analytical work it is the ratio of two weighings which is required. However, if an absolute calibration is desired it is only necessary to compare, by the substitution method, say the 10′ g. weight with a 10 g. weight the absolute value of which has been certified by the U.S. Bureau of Standards. From the comparison the absolute value of the 10′ g. weight of the analytical

Table 2

DATA FOR CALIBRATION OF WEIGHTS BY METHOD OF SUBSTITUTION

1 *Denomination of Wt. Being Calibrated, in g.*	2 *Wts. Used for Comparison*	3 *Sum of Value of Wts. of Column 2, in Units*	4 *Difference, in Units, Between Wt. Being Calibrated and Column 3*	5 *Value of Wt. Being Calibrated in Units: Column 3 + Column 4*	6 *Aliquot Portion of 9941.20*	7 *Correction in mg.; Column 5 minus Column 6*	8 *True Value, Relative; for Fract. Wts. in mg.; for Integral Wts. in g.*
0.01 (rider)	0.01′ (standard)	10 00 (assigned)	−0 06	9 94	9 94	0.00	10.0
0.01′ (standard)	0.01′ (standard)	10 00 (assigned)	0 00	10 00 (assigned)	9.94	+0.06	10 1
0.01″	0.01′ (standard)	10 00 (assigned)	−0.08	9 92	9.94	−0.02	10 0
0.02	0 01′ + 0 01″	19 92	+0 06	19.98	19.88	+0 10	20.1
0.05	0 02 + 0.01′ + 0.01″ + Rider at 10.0	49 84	−0 14	49.70	49.71	−0.01	50 0
0.1′	0 05 + 0 02 + 0.01′ + 0 01″ + Rider at 10.0	99 54	−0 23	99 31	99.41	−0.10	99.9
0.1″	0 1′	99 31	+0.19	99 50	99.41	+0.09	100 1
0.2	0 1′ + 0 1″	198 81	+0 48	199 29	198.82	+0.47	200 5
0.5	0 2 + 0 1′ + 0 1″ + etc.	497 64	−0 29	497 35	497 06	+0.29	500.3
1	0 5 + 0 2 + 0.1′ + etc.	994 99	−1.12	993 87	994 12	−0.25	0.9998
2′	1 + 0 5 + 0 2 + etc.	1988 86	−0.34	1988 52	1988.24	+0 28	2 0003
2″	2′	1988 52	+0 08	1988 60	1988 24	+0.36	2 0004
5	2′ + 2″ + 1	4970 99	−0.26	4970.73	4970 60	+0.13	5 0001
10′	5 + 2′ + 2″ + 1	9941 72	−0.52	**9941.20**	9941.20	0.00	10.0000
10″	10′	9941 20	−0.04	9941.16	9941 20	−0.04	10 0000
20	10′ + 10″	19882 36	−0.44	19881.92	19882 40	−0.48	19 9995
50	20 + 10′ + 10″ + etc.	49706.00	+0.82	49706.82	49706.00	+0.82	50.0008

set is calculated. Suppose in this manner the 10′ g. weight is found to have an absolute value of 10.00004 g. Obviously the absolute correction for the 10′ g. weight is + 0.04 mg. The correction for the 5 g. weight will be $4970.73 - \left(\frac{9941.20 - 0.04}{2}\right) = +0.15$ mg., and the absolute value of the 5 g. weight is 5.00015 g. In this way the absolute weights of the entire set may be calculated. (Absolute values have not been included in Table 2.)

Calibration of Weights by a Complete, Certified Set. Some laboratories possess a complete set of weights which have been certified by the Bureau of Standards. A certificate is furnished showing the true weight of every piece. If such a certified set is available each piece from the analytical set may be checked against the corresponding certified piece by the method of substitution. In this way we avoid the labor of calculating the values of all pieces on the basis of the arbitrarily assigned standard and the consequent possibility of accumulated errors. Furthermore, the corrections are at once on an absolute basis.

Preparation of Table of Corrections

To facilitate making the proper weights correction after weighing an object, it is well to prepare a table which, at a glance, will give the proper correction to apply. Two points in particular must be borne in mind in assembling the data for such a table. It is presumed that the weighing has been made in accordance with the rule laid down in the procedure for direct weighing (p. 52) and that therefore the smallest possible total number of pieces has been used. This is important because, for example, the weights correction for an object of 5 g. is different if the weighing is done with the single 5 g. weight from what it would be were the weighing carried out using two 2 g. weights and the 1 g. weight. Remember too that a "one-dot" weight is always selected in preference to a "two-dot" piece of the same denomination. In constructing the table, then, we follow the rule of avoiding an unnecessarily large number of weights, and of using the proper piece when a choice is possible.

Another point to keep in mind is that the correction for each denomination in Table 3 has been obtained to the hundredth milligram. In accord with the rules for significant figures, even though the table of corrections will list corrections only to the tenth milligram, the rounding off should be deferred until the algebraic summation has been made. To illustrate: say the individual corrections, in milligrams, for the 100′ mg., the 50 mg. and the 10′ mg. weights are, respectively, −0.10, −0.01 and +0.06. Should these corrections first be rounded off to the tenths and

Table 3

WEIGHT CORRECTIONS

MG. TO BE ADDED TO OR SUBTRACTED FROM TOTAL WEIGHT ON THE BALANCE

mg.	*0*	*10*	*20*	*30*	*40*	*50*	*60*	*70*	*80*	*90*
		0.1	0.1	0.2	0.1	0.0	0 1	0.1	0.2	0 1
100	−0.1	0.0	0.0	0.1	0.0	−0.1	−0.1	0.0	1.0	0.0
200	0 5	0.5	0.6	0 6	0.6	0.5	0.5	0 6	0.6	0 6
300	0.4	0.4	0.5	0.5	0 5	0.4	0.4	0.5	0.5	0.5
400	0.5	0.5	0 6	0.6	0.6	0.5	0.5	0.6	0.6	0.6
500	0.3	0.4	0.4	0.5	0.4	0.3	0.3	0 4	0 4	0.4
600	0.2	0.3	0.3	0.1	0.3	0.2	0.2	0 3	0.3	0.3
700	0.8	0.8	0.9	0.9	0.9	0.8	0.8	0.9	0 9	0.9
800	0.7	0.7	0.8	0.8	0 8	0.7	0.7	0 8	0 8	0.8
900	0.8	0.8	0.9	0.9	0.9	0.7	0.8	0 8	0.9	0.9
g.	*0*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
		−0.3	0.3	0 0	0.6	0 1	−0 1	0.4	0 2	0.8
10	0 0	−0.3	0 3	0.0	0 6	0 1	−0 1	0.1	0 2	0.8
20	−0 5	−0.7	−0 2	−0.5	0 2	−0.4	−0.6	−0 1	−0 3	0.3
30	−0.5	−0.7	−0.2	−0.5	0.2	−0 4	−0.6	−0 1	−0 3	0.3
40	−0.5	−0.8	−0 2	−0 5	0 1	−0.4	−0 6	−0 1	−0 4	0.3
50	0 8	0.6	1.1	0 9	1.5	1 0	0.7	1 2	1 0	1.6
60	0 8	0 6	1.1	0 9	1.5	1 0	0 7	1 2	1.0	1.6
70	0.3	0.1	0.6	0 4	1.0	0.5	0 2	0 8	0.5	1 1
80	0.3	0.1	0.6	0.4	1.0	0.5	0.2	0 8	0.5	1 1
90	0.3	0.1	0.6	0 3	0.9	0.4	0 2	0.7	0.5	1.1

then the algebraic addition made, the correction for a total weight of 160 mg. would be $-0.1 - 0.0 + 0.1 = 0.0$. However, if the addition is made first and the sum then is rounded off to the tenths, the resulting correction for 160 mg. is $-0.10 - 0.01 + 0.06 = -0.05$, or, rounded off, -0.1, which is the proper correction. Table 3 is the weights-correction table prepared from data taken from Table 2.

ERRORS IN WEIGHING

What has been presented in the foregoing sections emphasizes the fact that there are many sources of possible error whenever a weighing is made. The significance of several of them has already been evaluated; for example, that due to inequality of length of balance arms (pp. 54, 55), that due to buoyancy of the air (p. 55) and that due to inaccuracy of the weights (p. 57). Means of overcoming or minimizing such errors have been discussed. In addition, errors will result from weighing objects not at room temperature, or if uneven temperature prevails within the balance.

Still another cause for poor results comes from wiping the object, especially if made of glass or of porcelain, with a cloth, thereby imparting a static charge of electricity to the object. When this happens erratic results in the determination of the equilibrium point with the load are immediately noticed; in such cases the weighing cannot be completed until the electrical charge is dissipated, which may take several minutes.

It often happens that a substance being weighed becomes heavier even while the weighing is being carried out. This means that something is being taken up by the substance from the air. Hygroscopic materials take up water, and certain substances like calcium oxide take up carbon dioxide, with sufficient rapidity to make reproducible equilibrium points impossible. When this occurs it is best to place the approximately correct amount of weights upon the right pan before removing the object from the desiccator. When this has been done the object is placed on the left pan, the rider quickly adjusted and the equilibrium point determined at once.

Use of Balanced Watch Glasses. Weighing by Difference

In weighing a sample of a powdered material for analysis, either of two methods may be employed. Balanced watch glasses (pairs, which are of almost equal weight) may be used. With balanced watch glasses one does not need the equilibrium point with the pans empty. Rather the equilibrium point with the watch glasses in the pans is obtained. The weights (equal to the desired weight of the sample) are placed in the right watch glass and the powdered substance is added from a spoon to the left glass until slightly in excess of the weights. The exact weight then is determined as usual through proper placement of the rider and the determination of the equilibrium point with the load.

Powdered substances also may be weighed out by difference. This method, moreover, is useful especially in weighing sublimable or hygroscopic samples for analysis—that is, when the substance is likely to lose or to gain weight while being weighed. Several grams of the material are placed in a vial which is stoppered and weighed. Then holding the vial with cork-tipped forceps, the analyst removes the stopper with tongs and gently taps out a sample of appropriate size. The stopper is replaced and the vial again weighed. The decrease in weight represents the amount of sample obtained.

Questions and Problems

1. Name several factors which affect the sensitivity of the balance. Explain.
2. Explain how the sensitivity of a balance may be changed.
3. What objections are there to overloading a balance?

4. What advantages have the method of double-weighing and the substitution method over the direct method of weighing?
5. Under what circumstances is the buoyancy correction unimportant in weighing?
6. In weighing by the method of substitution should the tare (i.e., counterpoise) be of about the same density as that of the weights used? Why or why not?
7. An object when placed on the left-hand pan of a balance has an apparent weight of 18.2468 g. When transferred to the right-hand pan and weighed, the apparent weight is 18.2486 g. (a) What is the true weight of the object? (b) What is the ratio of the lengths of the balance arms? (c) In parts per million, how much do the lengths of the arms vary?
   Answer: (a) 18.2477; (b) 1.00000:1.00005; (c) 50.
8. A sample of a certain alloy weighs 56.8873 g. in air. Suspended by a wire and weighed in water the alloy weighs 49.1960 g. The wire immersed in water to the same depth weighs 0.3210 g. All weighings were made with brass weights. (a) Calculate the density of the alloy. (b) Calculate the true weight, *in vacuo*, of the alloy.
   Answer: (a) D = 7.1; (b) 56.8888 g.
9. Exactly 1.0000 g. samples of substances with densities of 0.25, 0.50, 1.00, 2.00 and 8.00 are weighed in air with brass weights. Calculate the differences between the weights in air and the corresponding weights *in vacuo*. Make a graph of these differences plotted against the densities.
10. A piece of platinum having a density of 21.37 weighs 5.0000 g. when weighed in air with a certain set of weights. If the platinum weighs 4.9981 g. *in vacuo*, what must be the density of the weights which were used?
    Answer: 2.8.
11. A platinum dish weighs 28.7654 g. in air when weighed with aluminum weights. Calculate its weight *in vacuo*.
    Answer: 28.7542 g.
12. The weight of a platinum object weighed in air with aluminum weights is greater than its weight *in vacuo*. The weight of an aluminum object weighed in air with platinum weights is less than its weight *in vacuo*. The weight of a brass object weighed in air with brass weights is the same as its weight *in vacuo*. Explain these statements.

Chapter 5

CALIBRATION OF VOLUMETRIC APPARATUS

PRECISE measurements of volume, usually of liquid, are made by the analyst almost as often as those of mass. The more commonly employed instruments for measuring volumes are the buret, the pipet and the volumetric flask. The first two usually are used to deliver a definite quantity of liquid while the last contains a given volume. Each is marked with etched lines by the manufacturer to designate the volume delivered by or contained in the apparatus. Just as in the case of the weights used with the analytical balance, it is probable that the number appearing on the volumetric flask, for example, is somewhat in error. If the flask is marked 500 ml. the probability is that it holds a little more or a little less than 500 ml. Therefore for the best work all such apparatus should be calibrated; that is, we ourselves should determine the capacity of the instrument as carefully as possible. Otherwise, every time we use the apparatus we introduce an error into our work, and frequently such errors exceed the errors inherent in the analysis.

The unit of volume is the liter (l.). The liter is that volume occupied by 1 kilogram of water at the temperature at which the density of water is greatest, namely, 3.98°, and at a pressure of 1 atmosphere. One-thousandth of the liter is a milliliter (ml.). The milliliter is almost but not quite identical with the cubic centimeter (cc.) which, of course, is the volume of a cube having an edge 1 centimeter in length. Originally it was intended that the two would be the same, but because of small experimental errors a difference between the two exists amounting to 28 parts per million, or 0.028 parts in 1000. (Prove this from the fact that exactly 1 ml. = 1.000028 cc.) This variation is so slight as to be insignificant in volumetric analyses where the expected precision usually is 1 part per 1000. Since the milliliter is the unit employed by the U.S. Bureau of Standards and since practically all apparatus is now labeled in terms of milliliters, it is preferable to the older usage of the cubic centimeter.

There are two reasons why any piece of volumetric apparatus is marked with a temperature reading as well as with the number of milliliters which it delivers or contains. Water, and its solutions, vary in density with change in temperature; thus a container which measures 100 ml. at 20° will not measure 100 ml. at other temperatures. Further-

more, glass expands with rising temperature, and this too would alter the capacity of the instrument. Almost all apparatus has a volume designated for 20°. If used at any other temperature we must make allowance for the change in volume which these two factors bring about.

Change of Volume of Solutions with Change of Temperature. The change in the volume of a solution due to a change in its temperature is greater the more concentrated the solution. However, in quantitative analysis one uses relatively dilute solutions. By the very definition of the term density, the increase or decrease in volume will always be in the ratio of the densities at the two temperatures. In the case of pure water the density at 20° is 0.99823 and at 25° is 0.99707. The difference, 0.00116 (in an average total of 0.99765 or approximately 1), is about 1.16 parts in 1000. Thus a quantity of water occupying a volume of exactly 1000 ml. at 25° would have a volume of 1000.00 − 1.16 = 998.84 ml. at 20°. A change of 5° in temperature would therefore introduce an error of more than 1 part per 1000. In the case of solutions the error usually is greater than the above; solutions of most electrolytes of concentrations around 0.1 *M* or 0.2 *M* will so vary in volume that an error up to 3 parts per 1000 occurs for a 5° change in temperature. It is necessary therefore, as a general rule, to maintain the temperature of our solutions within less than 5° of that at which the apparatus was calibrated, and preferably within 2°, if we wish to keep our precision within 1 part per 1000.

Change in Capacity of Glass Apparatus with Change of Temperature. The cubic coefficient of expansion of glass is 0.000025 per 1°. That is to say, for each change of 1° the glass apparatus will vary in capacity by twenty-five millionths of its previous volume. This may be expressed mathematically by the equation,

$$V' = V[1 + 0.000025(t' - t)] \tag{1}$$

where V′ and V are the final and initial capacities of the glass container at the final and initial temperatures t' and t respectively. For example, a flask which has a capacity of 1000 ml. at 20° will contain at 25° a volume of

$$V' = 1000[1 + 0.000025(25 - 20)] = 1000.13 \text{ ml.}$$

It is clear then that, since the above shows a variation of only slightly more than 0.1 part per 1000, a change of 5° does not introduce a significant error, except for the most precise work, as far as expansion or contraction of the glass apparatus is concerned.

Calibration of a Volumetric Flask

Suppose that we wish to calibrate a liter flask. We may have either of two ends in view. We may wish to learn the true volume which is contained by the flask when filled up to the mark on its neck, or, on the other

hand, we may wish to place a new etched line on the neck at that height which actually does indicate exactly 1000 ml. In either case we must have at hand a balance which is capable of weighing up to 2000 g.

First let us consider the determination of the true volume contained at 20° by a so-called 1000 ml. flask when filled to the graduation mark. The flask is thoroughly cleaned with cleaning solution, rinsed first with tap water and then three times with distilled water and dried.[1]

Procedure. Place the stoppered flask on the left-hand pan of the balance and add weights, or any metal pellets, copper shot for example, to the right-hand pan until an approximate balance is obtained, that is, until the equilibrium point is close to the mid-point on the scale. Remove the flask and replace with weights on the left-hand pan until the same equilibrium point is established. The sum of these weights represents the weight of the flask, inasmuch as this substitution method of weighing cancels out any errors that otherwise would result from inequality in length of the balance arms. Next carefully add distilled air-free water to the flask at room temperature, say 25°. It is well to add the last milliliter or two by means of a small pipet bringing the meniscus just tangent to the graduation mark of the flask. Be careful that no droplets adhere to the upper part of the flask. Replace the stopper and weigh flask and water, again by the substitution method. From the weight of the water itself the true volume of the flask is obtained from the density and temperature, corrections being made for buoyancy and glass expansion. The data of Column 6, Table 4, are convenient for this purpose.

Next, let us say that we wish to calibrate the flask so as to contain at a given temperature—for instance, 20°—a definite volume of liquid—for example, 1000 ml. After cleaning and drying the flask place it on the left-hand pan and, along with it, weights the sum of which is equal in grams to the number of milliliters of water the flask is to contain—in the present example, 1000 g. From an auxiliary set of weights, or with metal pellets, add a tare to the right-hand pan and determine the equilibrium point. Now remove all the weights, i.e., the 1000 g., from the left-hand pan. Do not add water as yet to the flask for to do so would require 1000 g. of water and would ignore the effects of density change (the temperature is not 20°), the buoyancy effect and the effect of contraction of glass. To compensate for these effects we must add weights to the left-hand pan. In the present case this amounts to 3.85 g., as may be seen from Table 4. (The compensating weight is always added to the pan with the empty flask since the figures in Column 6 are less than 1000.) After placing the 3.85 g. on the left-hand pan water is added to the flask until the original

[1] The drying may be accomplished quickly by rinsing the clean flask once or twice with a small amount of alcohol followed by a rinse with ether. Then insert a glass tube connected to a suction pump and draw cotton-filtered air into the flask to sweep out the ether vapor.

Table 4

CALIBRATION TABLE

WEIGHTS OF WATER, WEIGHED IN AIR WITH BRASS WEIGHTS AT TEMPERATURES FROM 15° TO 30°, WHICH MUST BE TAKEN TO INDICATE, IN GLASS CONTAINERS, A VOLUME OF 1000 ML. AT 20° (COLUMN 6)

Temp., °C.	*1* *Wt. of 1000 ml. Water in Vacuo g.*	*2* *Correction 1 (for Density) g.*	*3* *Correction 2 (for Buoyancy) g.*	*4* *Correction 3 (for Glass Contraction or Expansion) g.*	*5* *Sum of Corrections 1 + 2 + 3 (Compensating Weights) g.*	*6* *1000 − Sum of Corrections g.*	*Temp., °C.*
15.....	999.13	0.87	1.07	0.13	2.07	997.93	15
16.....	998.97	1.03	1.07	0.10	2.20	997.80	16
17.....	999.80	1.20	1.07	0.08	2.35	997.65	17
18.....	998.62	1.38	1.06	0.05	2.49	997.51	18
19.....	998.43	1.57	1.06	0.03	2.66	997.34	19
20.....	998.23	1.77	1.05	0.00	2.82	997.18	20
21.....	998.02	1.98	1.05	−0.03	3.00	997.00	21
22.....	997.80	2.20	1.05	−0.05	3.20	996.80	22
23.....	997.56	2.44	1.05	−0.08	3.41	996.59	23
24.....	997.32	2.68	1.05	−0.10	3.63	996.37	24
25.....	997.07	2.93	1.05	−0.13	3.85	996.15	25
26.....	996 81	3.19	1.05	−0.15	4.09	995.91	26
27.....	996.54	3.46	1.05	−0.18	4.33	995.67	27
28.....	996 26	3.74	1 05	−0.20	4.59	995.41	28
29.. . .	995 97	4 03	1 05	−0.23	4.85	995.15	29
30.....	995.67	4 33	1.05	−0.25	5.13	994.87	30

equilibrium point is established. The flask now contains that weight of water at 25°, namely, 996.15 g. which marks the height to which the glass flask must be filled at 20° to contain 1000 ml. A mark is etched with hydrofluoric acid at the level of the water meniscus.

Meaning of Table 4. The data of Table 4 are required to calibrate glass apparatus in order to correct for the change in density of water with change of temperature, for the buoyancy effect of air in weighing and for the expansion or contraction of glass with change of temperature from 20°. We have assumed, for the sake of illustration, that the temperature at which we are calibrating a flask is 25°. At this temperature the apparent weight of 1000 ml. of water as taken from Column 6 of Table 4 is 996.15 g. Since the weights which were removed from the pan after obtaining the original equilibrium point totaled 1000 g., the difference, or 3.85 g. (Column 5), represents our compensating weight and this must be added to the

left-hand pan. Obviously if we now add water to the flask until we re-establish the original equilibrium point we shall have added 996.15 g. of water to the flask, and this is the amount of water which must be taken at 25°, our working temperature, to indicate in glass a volume of 1000 ml. at 20°. (Weights corrections, since they appear only in the fourth, or sometimes the third, decimal place, need not be taken into account here where the total weight involved is so large. Neither is it necessary to ascertain equilibrium points better than approximately since an error of one scale division or so would cause a corresponding weight error of only a few milligrams, which in a total of about 1000 g., or even 100 g., is much less than 1 part per 1000.)

To comprehend fully the meaning of the data of Table 4, let it be restated that three considerations must be taken into account when we calculate the proper weight of water to be used in volumetric calibrations. These are: the density factor, the buoyancy factor and the glass expansion or contraction factor. We may now examine each of these.

Correction 1 (Column 2) is simply the density correction. Water at 4° has a density of unity and above this temperature, because of expansion of water, its density is less than unity. Thus above 4° the mass of water which will occupy a volume of 1000 ml. will be less than 1000 g.; the mass, or *in vacuo* weight, will be $1000d$, where d is the density at the higher temperature. The figures of Column 1 are the product of 1000 ml. and the density of water at the different temperatures. For example, the density of water at 25° is 0.99707; this multiplied by 1000 gives the figure in Column 1 for 25°, namely 997.07 g. This differs from 1000 g., the weight of a liter of water at 4°, by 2.93 g. It follows that this value, 2.93 g., and the others of Column 2, are the weights which must be subtracted from 1000 g. in order to obtain the weights of water *in vacuo* which at the indicated temperatures occupy 1000 ml. If the density correction were the only correction necessary, then for the calibration just outlined 997.07 g. of water would have been taken.

The second correction is for the buoyancy effect of air upon the water and the weights. Anything weighs less in air than *in vacuo*. The correction to be made is the difference between the two buoyancy effects which respectively are equal to the weights of air which are displaced by the water and by the weights. The water displaces of course almost exactly a liter of air, and a liter of air weighs approximately 1.19 g. (see p. 56, Chapter 4), depending upon atmospheric pressure, temperature and humidity. The volume of air displaced by the brass weights is equal to their mass, 997 g. in our example, divided by the density of brass, 8.4 (if copper shot were used as a tare, 8.9, the density of copper). This gives $997/8.4 = 119$ ml. This quantity of air weighs $(119)(0.00119) = 0.14$ g. This weight subtracted from 1.19 g. gives 1.05 g. as the buoyancy correc-

tion. (Incidentally, if this correction is added to Correction 1 and the sum subtracted from 1000 g. we would have that weight of water to be taken for calibrating at 25° a flask which subsequently was to be used at 25°.) These corrections, for buoyancy, are found in Column 3 of the table.

The third correction takes care of the expansion or contraction of the glass container (expansion or contraction, depending upon whether the calibration is carried out above or below 20°, the temperature taken by the Bureau of Standards as the standard temperature for calibrations). It already has been pointed out in equation (1) just how the capacity of a glass container changes as the temperature is varied. We saw that this does not introduce an error greater than 1 part per 1000 when the temperature differs by 5° or less from standard temperature. However, in the calibration of apparatus we should aim for the greatest possible precision. Correction 3 thus, while small (compare Columns 2, 3 and 4 of Table 4), should be included. It was shown previously (p. 66) that a glass vessel holding 1000 ml. at one temperature would contain 1000.13 ml. at a temperature 5° higher, an increase of 0.13 ml. Now 0.13 ml. of water having a density of 0.99707 weighs 0.13 g. This is Correction 3, which obviously must be subtracted for a working temperature which is 5° above standard, 20°. (Likewise the same figure, 0.13, is added for a working temperature which is 5° below standard; see Correction 3 of Table 4 for 15°.)

We may avoid the laborious process of making these three calculations by using Table 4 where the several corrections have been assembled for usually prevailing temperatures. From Column 6 one may obtain the weight of water which must be weighed in air with brass weights[2] at any temperature shown in the table in order to indicate a volume of 1000 ml. in a glass container at 20°. Column 5, giving the sum of all three corrections, tells us the number of grams to add to the left-hand pan as "compensating weights" previously mentioned. If the flask to be calibrated is not to contain 1000 ml., then a proportionate part of the numbers of Columns 5 and 6 apply; for example, to calibrate at 25° a flask to contain 500 ml. at 20°, the figure for Column 5 would be half of 3.85 or 1.93 g.

Calibration of a Pipet

Just as in the case of calibrating a flask, we may wish either to determine the true volume of the pipet as designated by its graduation mark, or we may wish to place upon the pipet a new mark so that a certain quantity of liquid will be delivered.

Procedure. In the first case we proceed as follows: After the pipet is cleaned so that it shows a uniform film after rinsing, fill by suction with

[2] A difference of only 0.01 part per 1000 results if copper shot are used as a tare instead of auxiliary brass weights; prove this.

distilled water at room temperature so that the meniscus is above the graduation mark. Quickly place the forefinger over the top in order to retain the liquid in the pipet. Hold the pipet in a vertical position over a beaker and carefully admit air by releasing the pressure of the finger, thus allowing the level of the water to fall until the meniscus is tangent to the mark. Remove any hanging droplet by touching the tip to the side of the beaker or by wiping with a piece of Kleenex tissue. Next run the water from the pipet into a clean, dried weighing bottle which has been weighed by the substitution method to the third decimal place. Allow the pipet to drain for about 15 seconds, then touch the tip to the inside surface below the ground-glass neck to remove the hanging drop. Do not blow or tap out the small amount of water remaining in the pipet tip. Weigh the bottle and water, again by the substitution method, and from the data of Table 4 calculate the true volume.

In the second case, to calibrate the pipet for the delivery of a predetermined volume, the procedure is somewhat different. Determine the true volume of the pipet exactly as described in the above paragraph. If this proves to be greater than the volume specified by the manufacturer, place a gummed label on the stem at a position somewhat below the etched mark; if the true volume is less than the nominal value, place the label somewhat above the etched mark. Determine the true volume of water delivered from this new marker. We now have two true volumes; one represents the volume delivered from the manufacturer's mark and the other the volume delivered from the gummed label. From the distance between these two marks and the true volumes corresponding to each, estimate by interpolation the position of a third mark, between the two, which should give the desired volume. Paste a new label at this point and make a new determination of the true volume delivered by the pipet from this level. Sometimes due to slight errors in interpolation it may be necessary to shift the final label slightly in order to secure the proper position for the desired definite volume. When the position has been accurately established substitute a permanent etched mark for the gummed label.

Calibration of a Buret

A buret may show deviations from the true volume at any position throughout its length. It therefore is necessary to check the buret at several points. For a 50 ml. buret it is usual to determine the true volume which is delivered at 10 ml. intervals.

Procedure. After the buret has been thoroughly cleaned, place distilled water at room temperature in the buret and lower the meniscus until it is tangent to the zero mark. See that no air bubble is in the buret tip and remove any hanging droplet. Then open the stopcock

slightly so that the water flows drop by drop into the weighing bottle which previously has been cleaned, dried, cooled and weighed with its stopper to the third decimal place (substitution method of weighing). When the meniscus has fallen exactly to the 10 ml. mark turn off the stopcock. Handling the weighing bottle with tongs, detach any hanging droplet by touching the buret tip to the inside surface of the weighing bottle below the ground-glass neck. Replace the stopper and weigh the bottle plus water to the nearest thousandth gram. The true volume delivered between the zero and 10 ml. mark is obtained, as usual, by dividing the weight of water by $\frac{1}{1000}$ of the figure found in Column 6 of Table 4 at the proper temperature. The difference between the volume so calculated and the buret reading, namely 10.00 ml., is the buret correction.

Refill the buret to the zero mark. The above procedure is now repeated except that water is withdrawn until the 20 ml. mark is reached. Then, after refilling the buret, 30 ml. is withdrawn and weighed; then 40 ml., and finally 50 ml. In every case the interval being calibrated should be run in duplicate and duplicate runs should check within 0.01 ml. After the data for all five intervals have been obtained construct a graph in which buret readings are plotted against the corrections. A sample set of data for the calibration of a buret are given in the following table.

Table 5

CALIBRATION DATA FOR A BURET TO BE USED AT 20°

1	*2*	*3*	*4*	*5*	*6*
Buret Reading, in ml.	*Weight of Water Delivered, in g.*	*Temp. of Water, in °C.*	*Corrected "Density," Col. 6, Table 4*	*True Volume, in ml.*	*Buret Correction, in ml.*
10.00.....	9.982	25.0	0.99615	10.02	+0.02
20.00.....	19 966	25.0	0.99615	20.04	+0.04
30.00	29.902	25.2	0.99610	30.02	+0 02
40 00.....	39.820	25.0	0.99615	39.97	−0.03
50.00.....	49.725	24.8	0.99619	49.92	−0.08

In any calibration of volumetric apparatus all weighing bottles must, of course, be handled with tongs. In making duplicate determinations time can be saved by always having one weighing bottle in the oven at 105° for drying and then in the desiccator for cooling, during the time that the other weighing bottle is being weighed. Note that weighings are made only to the third decimal place. Burets can be read only to the hundredth milliliter and if, during a calibration, we determine the weight of water to the thousandth gram (and the corresponding volume to the

thousandth milliliter) and then round off the volume to the hundredth place we drop the last, doubtful figure and thus have the true volume, theoretically at least, with no doubtful figure.

Problem. A flask filled to the mark at 24° contains 996.10 g. of water when weighed in air with brass weights. (a) What is its volume at 24°? (b) What is its volume at 20°?

Solution. (a) From Table 4, the mass of water which in air at 24° weighs 996.10 g. is 996.10 + 1.05 = 997.15 g. At 24° the mass of 1 l. of water is 997.32. Therefore the volume of the flask at 24° is $\frac{997.15}{997.32}$ = 999.83 ml.

Or, part (a) may be solved directly from Table 4 as follows: Because the capacity is wanted for the same temperature as that at which the calibration was carried out, Correction 3 is not included. The volume of the flask at 24° is 996.10 + Correction 1 + Correction 2. The sum of these corrections at 24° is 3.73. Thus the volume at 24° is 996.10 + 3.73 = 999.83 ml.

(b) If the flask contains 999.83 ml. at 24° we see by Column 4 of Table 4 that it will contract in capacity to an extent of 0.10 ml. when the temperature is 20°. Therefore the flask will have a volume of 999.73 ml. at 20°.

Or, part (b) may be solved directly from Table 4 in the following manner. The sum of all three corrections, Column 5 of Table 4, at 24° is 3.63. Therefore the volume of the flask at 20° will be 996.10 + 3.63 = 999.73 ml.

Problems

1. What weight of water must be used at 27° to locate the mark on a flask so that it will serve as a calibrated flask of 1000 ml. capacity at 20°?
   Answer: 995.67 g.
2. What weight of water must be used at 30° to locate the mark on a flask so that it will serve as a calibrated flask of 500 ml. capacity at 20°?
   Answer: 497.44 g.
3. A flask is filled to the mark by adding 498.50 g. of water at 22°. What is the capacity of the flask if used at 22°?
   Answer: 500.13 ml.
4. A flask which is supposed to be of 1 l. capacity is filled to the mark with water at 18° weighing 997.51 g. (a) What is its volume at 18°? (b) What is its volume at 20°?
   Answer: (a) 999.95 ml.; (b) 1000.00 ml.
5. A solution is standardized by titration in a glass buret and found to be 0.1015 *N*. The temperature is 20°. Later it is restandardized but the temperature is 26°. What normality should be obtained in the latter determination?
   Answer: 0.1014 *N* if the standardization was primary.

Chapter 6

VOLUMETRIC ANALYSIS. FUNDAMENTAL PRINCIPLES

ANALYSES by volumetric methods are based upon the interaction of the constituent to be determined with a definite volume of a solution of known concentration, called a *standard* solution. The determination of the concentration of the latter solution is known as the standardization of the solution. The addition of an equivalent quantity of one solution to a definite amount of another and the measurement of the volume employed is called a *titration*. The point at which an equivalent quantity of the one solution has been added from the buret is recognized by the use of an indicator. This is a substance which, present in small amount in the solution being titrated, will reveal, usually by a change in color, the point at which enough of the titrating solution has been added to complete the desired chemical reaction. Indicators thus mark the *end point* of a titration. Ideally the end point should coincide with the *equivalence point*, that is, the *stoichiometric point*, at which chemically equivalent quantities of the reacting substances have been brought together. This is the object of all titrations, and a suitable indicator for a given titration is one which will give the stop signal when chemically equivalent quantities have reacted. As will be shown later, the end point and the stoichiometric point do not always coincide exactly but for a feasible titration the two must closely approach one another.

Methods of Expressing Concentration. The concentration of a solution may be expressed in several ways, all of which reveal the quantity of solute per unit volume or per unit weight of solution or of solvent. Obviously one method is to state the weight of solute per liter or milliliter of solution. For example, we might have a solution of sodium chloride containing 50 g. of the salt in a liter of aqueous solution. Again the concentration may be stated in terms of weight of solute per unit weight of solution, as 50 g. of sodium chloride per 1000 g. of solution. Such a solution would be a 5 per cent solution. This would be not quite the same as the former since the volume of a given amount of solvent will change somewhat upon dissolving the solute. Another method essentially the same as this is to give the specific gravity and the weight percentage of the solute present. The statement that a sulfuric acid

solution has a specific gravity of 1.84 and consists of 96 per cent H_2SO_4 by weight is unambiguous since there is only one concentration of sulfuric acid compatible with these data. Another common expression of concentration is per cent by volume. A solution of 10 ml. of alcohol per 100 ml. of solution is said to be 10 per cent alcohol by volume.

Although all of the above means of denoting the concentration are frequently employed, none of them meets the particular needs of volumetric analysis so well as a method based upon the interacting chemical units instead of upon absolute weight or volume percentages. If it were true that 1 g. of a substance always reacted with, say, 1 g., or 2 g., of another substance, then it would be advantageous to make up all of our standard solutions with a given number of grams of solute per unit volume of solution. The fact is, however, that substances react with one another in the ratio of whole numbers of molecules.

Molar Solutions. If standard solutions were made up so as to contain equal numbers of molecules per liter of solution it follows that all such solutions, if they react with one another, would do so in the ratio of small, whole number volumes. This would make matters simpler than if all the solutions contained the same number of grams per unit volume of solution. Since all gram molecular weights contain the same number of molecules we may prepare such *molar solutions* by dissolving per liter of solution the molecular weight of the solute expressed in grams. That is to say, a molar solution is one which contains 1 gram molecular weight, or 1 *mole*, of solute in 1 l. of solution. For example, 58.45 g. of sodium chloride, 98.08 g. of hydrogen sulfate and 98.00 g. of hydrogen phosphate all give, if dissolved in a liter of solution, molar solutions. However, even the molarity system is not always the most convenient means of expressing the concentrations in volumetric analysis. It would be if it were true that chemical reactions always involved equal numbers of molecules. But since, for example, hydrochloric acid and sodium hydroxide react molecule for molecule, while sulfuric acid and sodium hydroxide react, for complete neutralization, in the ratio of one molecule to two, it would be better if we devise a system in which two solutions having concentrations of the same numerical value will react volume for volume. This may be accomplished if we employ the normality system for concentrations.

Normal Solutions. It has been stated that if two substances react at all they do so by whole numbers of molecules. But what is it which determines whether the ratio in which molecules react will be one to one, or one to two, or something else? In the case of an acid reacting with a base the answer lies in the number of hydrogen and hydroxyl ions per molecule. An acid like sulfuric which ionizes to yield two hydrogen ions obviously may react with two molecules of sodium hydroxide which

dissociates to give only one hydroxyl ion since the essential reaction of neutralization is

$$H^+ + OH^- \rightarrow H_2O$$

It follows that 1 l. of a solution of sulfuric acid containing half as many solute molecules as a liter of sodium hydroxide solution would just neutralize the latter because the sulfuric acid would yield the same number of hydrogen ions as the base would furnish of hydroxyl ions. Thus a 0.5 molar solution of sulfuric acid is exactly equivalent to a 1 molar solution of sodium hydroxide. Since they are equivalent there must be a means of designating such equivalence. This is accomplished by saying that the above are both 1 *normal* solutions. A *normal solution* is defined as a solution 1 l. of which contains, or will replace or combine with, 1 *gram atomic weight* of hydrogen (1.008 g.) or its equivalent. Such a quantity of solute is called its *gram equivalent weight*. That is to say, the gram equivalent weight of any acid, base or salt is the weight of the substance in grams which will react with 1.008 g. of hydrogen or hydrogen ion, with 35.46 g. of chlorine or chloride ion, etc., and the normal solution is one containing 1 gram equivalent weight of solute per liter of solution.

It is easy to compute the equivalent weight of electrolytes. A few examples will suffice to illustrate. Hydrochloric acid has a molecular weight of 36.46 to which hydrogen contributes 1.008; therefore the use of 36.46 g. of hydrogen chloride will furnish 1.008 g. of hydrogen, and the gram molecular weight and the gram equivalent weight are identical, namely, 36.46 g. Sulfuric acid, molecular weight 98.08, will yield two hydrogen ions per molecule; therefore 98.08 g. furnish 2.016 g. of hydrogen ion or 49.04 g. furnish 1.008 g. The gram equivalent weight of sulfuric acid is thus 49.04 g. The gram equivalent weight of bases may be calculated on the basis of the number of hydroxyl ions from each molecule since one hydroxyl ion is equivalent to one hydrogen ion. For sodium hydroxide, molecular weight 40.01, the gram equivalent weight is 40.01 g.; for calcium hydroxide, molecular weight 74.10, the equivalent weight is 37.05. In the case of salts one may judge matters by the number and valence of either of the ions which the salt yields. If it dissociates to give one univalent ion of a given sign the molecular weight and the equivalent weight are the same, as in the case of sodium chloride, 58.45. But sodium sulfate, molecular weight 142.1, yields two univalent positive ions, which are equivalent to two hydrogen ions, and its gram equivalent weight is therefore 71.05 g. Aluminum sulfate, molecular weight 342.1, would by the same reasoning have an equivalent weight equal to one-sixth of its molecular weight, or 57.02.

The terms milliequivalent weight, *meq.*, and gram milliequivalent

weight are often used. As the term implies, the meq. of a substance is its equivalent weight divided by 1000. Thus the meq. of NaOH is 0.04001 and its gram meq. is 0.04001 g.

Objection is sometimes raised to the normality system of designating concentration because the equivalent weight of a substance may vary according to the particular reaction which it undergoes. For example, the equivalent weight and the molecular weight of sodium carbonate are the same if the reaction proceeds according to the equation

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

but the equivalent weight is only half the molecular weight if conditions are such that the reaction is

$$Na_2CO_3 + 2HCl = H_2CO_3 + 2NaCl$$

Furthermore, the equivalent weight of potassium permanganate, which as a salt evidently is identical with its molecular weight, is, as we shall see later, a fifth of the molecular weight when this substance acts as an oxidizing agent in an acidic environment, and is a third of the molecular weight when it functions as an oxidant in a basic solution. However, the variability of the value for the equivalent weight of many substances, instead of being a source of confusion, is actually a means by which one comes to a quick understanding of the fundamental principles of equivalence. It is only necessary to consider the particular chemical reaction which the reagent is undergoing and to ascertain therefrom the number of hydrogen equivalents involved in the reaction. This number, divided into the molecular weight of the acid or base or salt, yields the equivalent weight. The advantage in volumetric analysis of the volume for volume relation when the normality system is used far outweighs the simplicity which is sometimes claimed for the more primitive molarity system; furthermore, the latter does not remove all ambiguity. In many cases it would be open to doubt as to what is meant by a molar solution unless some explanatory note were given. For example, a mole of water is not 18 g. unless the formula of water is H_2O and *not* $(H_2O)_x$. Also the mole of a salt which forms one or more hydrates obviously may be any of several values.

Standard Solutions and Standardizations

A *standard solution* is one of definite and known concentration. The concentration is usually designated in terms of the normality of the solution. If the solution contains 1 gram equivalent weight of the solute per liter of solution it is normal, 1 *N*. A solution which contains one-tenth of a gram equivalent weight of solute per liter is 0.1 *N*. Thus 40 g.

of sodium hydroxide in a liter of solution makes a 1 *N* solution, 4 g. per liter gives a solution which is 0.1 *N*, and 0.2 g. per liter makes the solution 0.005 *N*, etc. A standard solution often may be prepared in either of two ways. The proper amount of solute may be weighed exactly and dissolved in a carefully measured volume of solution (by using a volumetric flask). Or the solution may be made up using the approximately correct quantity of solute and solution and the exact value of the normality then determined by a process called standardization.

To illustrate the first method, assume that a tenth-normal solution of sodium chloride is wanted. It may be prepared by weighing 58.45/10, or 5.845 g. of pure dry sodium chloride, dissolving this in pure water, transferring quantitatively to a 1 l. volumetric flask, diluting to the mark and shaking. This involves the somewhat troublesome task of weighing the exact quantity, 5.845 g. This method cannot be employed if the solute is hygroscopic or if it cannot be obtained in a pure state.

In the second, more commonly employed method, an amount of the solute close to the calculated quantity is weighed on a trip balance—for example, about 4 g. of sodium hydroxide—and dissolved in roughly 1 l. of solution. The solution so prepared will not be 0.1000 *N* but nearly so. Usually it is not important that the standard solution be exactly 0.1000 *N*, 0.01000 *N*, etc., but only that the solution be close to the desired normality and that its exact normality be known. The exact normality of the solution is determined by titrating either against a suitable quantity of a "standard" (*primary* standardization) or against a solution the exact normality of which is already known (*secondary* standardization). If a solution of a certain definite normality—for example, exactly 0.1000 *N*—is desired, a slightly more concentrated solution is made up and standardized. Next it is diluted with water to the extent calculated to establish the exact desired normality and then restandardized (see p. 83).

Primary Standardization. A *standard* is a substance which will react quantitatively with the solution to be standardized in such a manner that the result of the titration may be used to calculate the normality of that solution. A standard must meet certain criteria.

1. The compound must be above 99.9 per cent pure, or of definitely known composition. Usually it is a solid.

2. It should be a stable compound which maintains a constant composition in contact with air.

3. It should undergo drying at 105° without change in its composition.

4. It must be capable of accurate weighing. For example, it must not be hygroscopic and should not be easily sublimated, nor should its physical state be too fluffy.

5. It should dissolve readily in water or in other suitable solvents.

6. It must react with the solution to be standardized quantitatively, according to one invariable reaction.

7. It should have a fairly large equivalent weight. Since almost all student burets are of 50 ml. capacity a titration should not exceed this volume of solution and usually will run between 30 and 40 ml. This means that there is a definite upper limit for the number of gram milliequivalent weights of standard that may be used. If the meq. of the standard is small the actual weight appropriate for the titration of an approximately 0.1 *N* solution may be less than 200 mg., which means, when it is remembered that the error in weighing a substance may amount to 0.2 mg., that a relative error of more than 1 part per 1000 would be introduced.

After a standard meeting the above requirements has been chosen, the quantity necessary for a titration of 30 to 40 ml. of solution must be calculated. As is true in so many cases, there are long methods and a short way to make the calculation. It is *always* true that the amount of standard needed is equal to the product of three factors, namely: the approximate volume in liters (of the unknown solution) suitable for the titration, the approximate normality of that solution and the gram equivalent weight of the standard. No shorter method of calculation is possible. To illustrate: if a solution of sodium hydroxide which is about 0.1 *N* is to be standardized by titrating it against benzoic acid as the standard, the weight of benzoic acid necessary for a titration involving around 30 ml. of the base is

$$(^{30}/_{1000})(0.1)(122) = 0.366 \text{ g.}$$

Similarly, if sodium carbonate is to be used to standardize a 0.2 *N* solution of hydrochloric acid one should weigh out about

$$(^{30}/_{1000})(0.2)(^{106}/_{2}) = 0.318 \text{ g.}$$

The above type of calculation illustrates a perfectly general method for the reason that, since 1 l. of 1 *N* solution contains 1 gram equivalent weight of solute, 30 ml. of approximately 0.1 *N* solution contains about $^{30}/_{1000}$ of 0.1 of 1 gram equivalent weight. Therefore about $^{30}/_{1000}$ of 0.1 of a gram equivalent weight of the standard will be required for the reaction taking place during the titration.

It must be emphasized that although only a rough calculation should be made to ascertain the quantity of standard suitable for the titration and that the amount actually weighed out need only be somewhere near this calculated quantity, the weighing must be made exactly and to the fourth decimal place. The sole object of the standardization is to learn the normality of the solution with a possible error, as a rule, of not over 1 part per 1000. Therefore the standard must be weighed to the fourth decimal place and the buret must be read to the hundredth milliliter.

One should avoid discarding a weighed portion of standard if it happens to be somewhat more than the calculated amount—for example, 0.366 g. in the case of the benzoic acid–sodium hydroxide titration cited above—for it is obvious that if the base is close to 0.1 N it would require

$$(^{50}/_{1000})(0.1)(122) = 0.61 \text{ g.}$$

of benzoic acid to render refilling of the buret very likely.

The standard may be weighed, of course, either by difference or by using balanced watch glasses (see p. 63). If the titration is to be carried out in an Erlenmeyer flask the former is preferable because of the ease of transferring the standard from the weighing bottle or vial to the flask. If a beaker is used for the titration it is better to use balanced watch glasses for several reasons. First, it is a simpler matter to weigh out a quantity of standard between the upper and lower limits of the amount wanted, i.e., a quantity which will require between 30 and 50 ml. of solution from the buret. Secondly, the quantitative transfer of the standard to the titrating beaker is accomplished without loss simply by lifting with tongs the watch glass containing the accurately weighed standard and carefully placing it within the titrating beaker. The solvent then is added and the titration completed without removing the watch glass. Another advantage of this procedure is that stirring may be effected during the titration through rocking the watch glass by touching first one side and then the other with a glass rod. This diminishes the amount of carbon dioxide introduced from the air, an occurrence which happens if the solution is too vigorously agitated with a stirring rod. The absorption of carbon dioxide is objectionable in acid-base titrations when an indicator such as phenolphthalein is used (see p. 125). Sometimes an analyst uses a camel's-hair brush to sweep the material from the watch glass to the titrating vessel, but, while this procedure is safe in experienced hands, it involves the possibility of loss unless utmost caution is taken to dislodge all particles from the brush.

Calculation of Exact Normality. When the proper amount of the standard has been weighed and transferred to the titrating flask and the titration completed, the volume of the solution used is read, to the hundredth milliliter, from the buret. The calculation of the normality is quite simple and one should avoid becoming involved in unnecessarily long computations. An example will illustrate the point. Suppose a solution of sodium hydroxide approximately 0.1 N has been standardized against benzoic acid weighing 0.4134 g., and that the end point for the titration was 33.52 ml. From these data it is possible to calculate the normality of the base by carrying out the following logical but unnecessary number of steps[1]:

[1] Some psychologists claim that it is poor pedagogy to illustrate a wrong, or an undesirable, method. However, the involved calculation of normality here illustrated is

1. Compute the grams of benzoic acid equivalent to 1 l. of sodium hydroxide.

2. Compute the grams of sodium hydroxide equivalent to the grams of benzoic acid of step 1.

3. Divide the weight of sodium hydroxide of step 2 by the equivalent weight of sodium hydroxide. This will give the number of gram equivalent weights of sodium hydroxide per liter of sodium hydroxide solution and therefore is the normality of the solution.

In the case at hand these calculations are, in order:

$$\text{Step 1.} \quad \frac{0.4134}{33.52}(1000) = 12.33 \text{ g. } C_6H_5COOH$$

$$\text{Step 2.} \quad \frac{40.01}{122.1}(12.33) = 4.041 \text{ g. NaOH}$$

$$\text{Step 3.} \quad \frac{4.041}{40.01} = 0.1010 = \text{Normality of NaOH}$$

The above computation is more quickly made if one realizes that the normality of the titrated solution *always* must be

$$(1) \quad N \text{ of solution titrated} = \frac{\text{g. of standard} \div 1 \text{ l. of unknown solution}}{\text{equivalent weight of standard}}$$

From the data used in the previous illustration this yields:

$$N \text{ of NaOH solution} = \frac{\frac{0.4134}{33.52}(1000)}{122.1} = 0.1010$$

Obviously this shorter calculation merely eliminates the multiplication by 40.01 in step 2 and the subsequent division by 40.01 in step 3 of the longer method.

Equation (1) must yield the normality. There should be no confusion over the fact that we divide one set of numbers pertaining to the standard (here, benzoic acid) by another number also pertaining to the standard and arrive at a quotient (the normality) pertaining to the unknown solution (here, sodium hydroxide). If one contends that this quotient, 0.1010, represents the normality of a hypothetical benzoic acid solution it need only be borne in mind that such a benzoic acid solution would be one of which a liter was exactly equivalent to a liter of the sodium hydroxide solution. Therefore it would, of necessity, have the same normality as the sodium hydroxide solution. Equation (1) thus is valid for the calculation

so common among students of elementary quantitative analysis that it is believed best to contrast this method with the shorter, recommended method which follows (Equation (1)).

of the normality of the unknown solution and it will be found, in the chapter on oxidation and reduction, that this equation is applicable to the calculation of the normality of those solutions as well as to solutions of acids and bases and salts. It should be mentioned that primary standardizations are usually carried out in triplicate.

Secondary Standardizations. It has been mentioned already that the normality of a solution may be determined by means of a secondary standardization. That is to say, if a standard solution of hydrochloric acid, for example, is available, the normality of a solution of a base may be determined by titration of the base against the acid. In any titration the product of the normality and the volume of the one solution must equal the product of normality and volume of the other. To illustrate, it is obvious that 100 ml. of 0.1 N base must be equivalent to 10 ml. of 1 N acid, so that $(100)(0.1) = (10)(1)$, or, in general,

$$NV = N'V' \tag{2}$$

Thus if 30.00 ml. of hydrochloric acid solution known to have a normality of 0.1089 were titrated with the sodium hydroxide solution already considered and the end point occurred at 32.35 ml. of NaOH, the normality of the base would be calculated as follows:

Base		*Acid*
$N \cdot V$	=	$N' \cdot V'$
$N(32.35)$	=	$(0.1089)(30.00)$
N	=	0.1010

This type of standardization is called secondary because the normality of the unknown is determined by titrating against a solution which itself was standardized against a primary standard. Secondary standardizations are subject to two sources of error: in addition to any error made in the actual titration of the unknown solution, those errors acquired during the primary standardization of the hydrochloric acid, in the case at hand, will be carried along and included in the normality of the unknown, here the sodium hydroxide. Accordingly, it is customary, if two good checks are obtained in secondary standardizations, to make the determination only in duplicate. Since the errors, determinate and indeterminate, in every standardization may become additive, secondary standardizations should be avoided when highest accuracy is desired.

It should be emphasized that in the equation, $NV = N'V'$, the product of the normality and the volume, in milliliters, gives the number of gram milliequivalent weights of the substance. We know, for example, that 1000 ml. of 1 N solution contains 1 gram equivalent weight of solute, which is to say 1000 gram milliequivalent weights; and the product, NV, is $(1)(1000) = 1000$. Similarly, 50 ml. of 0.2 N solution gives the

NV product: (0.2)(50) = 10 or 10 gram milliequivalent weights.[2] Remembering this, such problems as the following become simple to solve.

Problem. A sample of oxalic acid, $H_2C_2O_4$, weighing 0.2268 g. is titrated against 0.2000 *N* NaOH solution, 25.14 ml. being required. Calculate the purity of the oxalic acid.

Solution. (0.2000)(25.14) = 5.028 gram meq. NaOH used. Thus there must be 5.028 gram meq. $H_2C_2O_4$ in the sample. The gram meq. of $H_2C_2O_4$ is 0.09004/2 g. or 0.04502 g. Therefore

$$(5.028)(0.04502) = 0.2264 \text{ g. } H_2C_2O_4$$

$$\frac{0.2264}{0.2268}(100) = 99.8\% \text{ pure}$$

Of course the last two of the above three steps may be combined.

Another way of looking at the above problem is from the standpoint of equation (1) from which we have by substituting in the equation

$$0.2000 = \frac{(0.2268X)(1000)}{25.14} \div 45.02$$

where X is the purity of the oxalic acid. Solving, we obtain

$$X = 0.998 \text{ or } 99.8\%$$

Dilution of Solutions to a Definite Normality. Sometimes it is desired to prepare a standard solution of a definite normality. Often it is impossible to weigh exactly the proper amount of solute as, for example, in the preparation of sodium hydroxide solution where the solute is hygroscopic. In any event the weighing of a definite quantity of a substance to the tenth milligram is troublesome; it usually is simpler to prepare a solution of slightly greater concentration than desired and then to dilute it to the proper concentration. To illustrate, if an exactly 0.1000 *N* solution of sodium hydroxide is to be prepared, the solution mentioned in the preceding section having a normality of 0.1010 may be utilized. Again equation (2) will serve for calculating the dilution necessary. If we wish 1 l. of 0.1000 *N* solution the question is simply this: How much of the 0.1010 *N* solution must be taken and diluted to 1000 ml. in order that the resulting solution will be exactly 0.1000 *N*?

$$N \cdot V = N' \cdot V'$$
$$0.1010V = (0.1000)(1000)$$
$$V = 990.1 \text{ ml.}$$

Therefore if 990.1 ml. of the 0.1010 *N* solution is diluted to 1000 ml. the resulting solution will be exactly 0.1000 *N*. After making such dilutions the new solution should be standardized in order to confirm the expected normality.

[2] The terms milliequivalent, milliequivalent weight and gram milliequivalent weight are often used interchangeably.

Dilution of Concentrated Solutions of Common Reagents

The analyst often finds it necessary to prepare solutions of common reagents like sulfuric, nitric, hydrochloric and acetic acids, and ammonium hydroxide from the concentrated solutions purchased from the manufacturer. The bottles containing these concentrated solutions are labeled with the specific gravity and the percentage by weight of the constituent. From these data the normality of the concentrated solution may be roughly calculated and by equation (2) the volume to be taken to prepare a more dilute solution may be computed. Table 6 gives the data for the common acids and for ammonium hydroxide.

Table 6

Concentrations of Common Laboratory Reagents

Reagent	*Sp. Gr.*	*Wt. %*	*g./ml.*	*N.*
H_2SO_4	1.84	96	1.77	36.1
HCl	1.19	36	0.43	11.7
HNO_3	1.42	69	0.98	15.6
$HC_2H_3O_2$	1.06	99	1.05	17.5
NH_4OH	0.90	28 (NH_3)	0.25	14.8

The figures of the third and fourth columns of the table may be calculated from those of the first two columns. This may be illustrated with the case of H_2SO_4. The specific gravity is 1.84, which means that a milliliter of the concentrated acid weighs 1.84 times as much as a milliliter of water, or 1.84 g. Since 96 per cent or 0.96 of the concentrated solution is hydrogen sulfate, the remainder being water, $(0.96)(1.84) = 1.77$ g. of H_2SO_4 is in 1 ml. of the solution. A liter of the solution then contains 1770 g. of H_2SO_4. This divided by the gram equivalent weight, or $^{1770}/_{49} = 36.1$, gives the normality of the concentrated acid.

If one wished to prepare 1000 ml. of a 0.5 N solution the volume of concentrated acid necessary obviously would be

$$N \cdot V = N' \cdot V'$$
$$36.1V = (0.5)(1000)$$
$$V = 13.9 \text{ ml.}$$

That is, if 13.9 ml. of the concentrated sulfuric acid is diluted to 1000 ml. the resulting solution would be 0.5 N. The exact normality, to four significant figures, then could be determined by standardization.

Problems

1. How many grams of each of the following substances are necessary to prepare the solutions indicated, assuming in each case that the acid resulting after dissolving is to be completely neutralized? (a) 1 l. of 0.5000 N $HC_2H_3O_2$.

(b) 500 ml. of 0.1000 *N* H_2SO_4. (c) 100 ml. of 0.2000 *N* acid made from dissolving P_2O_5 in water. (d) 1 l. of 0.5000 *N* $NaHSO_4$.

Answer: (a) 30.03. (b) 2.452. (c) 0.4732. (d) 60.03.

2. One mole of the alum, $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ contains how many (a) moles of water; (b) grams of water; (c) gram atomic weights of aluminum; (d) gram molecular weights of NH_3; (e) grams of oxygen?

Answer: (a) 24; (b) 432.38; (c) 2; (d) 2; (e) 640.

3. An aqueous solution of hydrochloric acid has a specific gravity of 1.120 and is 23.80 per cent HCl by weight. Calculate the normality of the solution.

Answer: 7.31 *N*.

4. Two solutions of sulfuric acid are available. One is 0.2000 *N* and the other is 0.2500 *N*. How many milliliters of the two should be brought together in order to prepare 1000 ml. of a solution about 0.2222 *N*? (Hint: use the equation, $NV + N'V' = N''V''$.)

Answer: 556 ml. of 0.2000 *N* plus 444 ml. of 0.2500 *N*.

5. What must be the normality of a potassium hydroxide solution 100 ml. of which, added to 250 ml. of a 0.1500 *N* KOH solution, will give a resulting solution which is 0.2000 *N*?

Answer: 0.3250 *N*.

6. A sample of 0.1928 g. of pure, dry oxalic acid is used to standardize a sodium hydroxide solution. If 32.82 ml. of the base is necessary in the titration what is the normality of the sodium hydroxide?

Answer: 0.1305 *N*.

7. How many milliliters of the sodium hydroxide solution of problem 6 would be needed to titrate a sample of 0.6060 g. of pure, dry potassium acid phthalate, $KHC_8H_4O_4$?

Answer: 22.74 ml.

8. What is the normality of a solution of potassium hydroxide of which 29.16 ml. is equivalent to 40.08 ml. of a potassium tetroxalate solution made by dissolving 4.237 g. of the $KHC_2O_4.H_2C_2O_4.2H_2O$ in water and diluting to 500 ml.?

Answer: 0.1371 *N*.

9. Calculate the equivalent weight of an acid of which 0.9250 g. is equivalent to 40.00 ml. of a sodium hydroxide solution if 5.00 ml. of the base is equivalent to 0.05025 g. of Na_2CO_3.

Answer: 122.1.

10. A sample of 0.3223 g. of calcite, $CaCO_3$, is dissolved by gently heating in 100.0 ml. of 0.1000 *N* HCl. After the reaction has ceased the excess acid is titrated with 0.2000 *N* NaOH, 18.51 ml. being required. Calculate the per cent purity of the calcite.

Answer: 97.8%.

11. A mixture of pure sodium carbonate and pure calcium carbonate weighs 0.3000 g. A volume of 40.80 ml. of 0.1401 *N* acid is necessary to neutralize exactly the mixed carbonates. Calculate the per cent of each present in the mixture.

Answer: 84% Na_2CO_3; 16% $CaCO_3$.

Though four significant figures are given in the data of this problem the answers are limited to two significant figures. Why?

Chapter 7

NEUTRALIZATION

THE REACTION between an acid and a base essentially consists of the combination of hydrogen ions with hydroxyl ions to form water. Such reactions are known as *neutralization* reactions. According to classical theories an acid is a substance which, in solution, furnishes hydrogen ions, and a base is one which furnishes hydroxyl ions. A strong acid or base is one which is practically completely dissociated in aqueous solution, while a weak acid or base is one which is only slightly ionized.

Brönsted[1] extended the concept of acids and bases in order to take into account their variations in strength when dissolved in different solvents and the part played by a particular solvent in ionization. According to the Brönsted concept an acid is defined as a substance which furnishes a proton (a positively charged hydrogen atom), that is, gives up a proton or is a proton donor. A base is defined as a substance which accepts a proton, that is, combines with a proton or is a proton acceptor. These definitions of an acid and a base may be summed up in the equation,

$$\underset{\text{acid}}{HA} \rightleftarrows \underset{\text{proton}}{H^+} + \underset{\text{base}}{A^-}$$

If the above reaction is followed by a combination of H^+ and the solvent, then the solvent is functioning as a base.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftarrows \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{A^-}$$

Here water acts as a base since water accepts a proton to form the hydronium ion, H_3O^+ (also called the oxonium ion). From the following equations for reactions which may take place in aqueous solution it is evident that a given substance may act sometimes as an acid and at other times as a base.

(a) $H_2O \rightleftarrows H^+ + OH^-$
(b) $H_3O^+ \rightleftarrows H^+ + H_2O$
(c) $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$
(d) $HCO_3^- \rightleftarrows H^+ + CO_3^=$

[1] Brönsted, *Rec. Trav. Chim.*, **42**, 718 (1923); *J. Phys. Chem.*, **30**, 777 (1926); *Chem. Revs.*, **5**, 231 (1928); *Trans. Faraday Soc.*, **25**, 59 (1929); Lowry, *Chem. & Ind.*, **42**, 43 (1923); Hall, *J. Chem. Education*, **7**, 782 (1930); *Chem. Revs.*, **8**, 191 (1931); *J. Chem. Education*, **17**, 124 (1940); Johnson, *J. Chem. Education*, **17**, 132 (1940).

In reaction (a) water acts as an acid and OH^- as a base, whereas in (b) water acts as a base and H_3O^+ as an acid. In reactions (c) and (d) the bicarbonate ion acts first as a base and then as an acid.

The classical concept of acids and bases places too much emphasis on aqueous solutions and obscures the mechanism of many reactions taking place in nonaqueous solutions. In terms of the Brönsted theory the mechanism usually appears as both simple and logical. However, the Brönsted theory does not specifically recognize that ions other than H^+ are solvated; neither does it specify the degree of solvation, since this is unknown. In the calculations of analytical chemistry the use of $[H^+]$, the concentration of hydrogen ion, leads to the same results as would the use of $[H_3O^+]$ or of $[(H_2O)_xH^+]$; therefore there is little advantage in employing the concept of the hydronium ion, and its usage is much more cumbersome.

Methods of Expressing Hydrogen Ion Concentration

Since neutralization reactions consist essentially of the interaction of hydrogen and hydroxyl ions, it is important to consider the methods of expressing the concentration of these ions. It will be recalled from studies in previous courses in chemistry that the equilibrium constant for any reversible reaction is derived from the application of the Law of Mass Action to the chemical equation for the reaction. It is equal to the product of the concentrations of the substances formed (expressed in moles per liter) raised to a power represented by the coefficients of the molecules (or ions), all divided by the product of the concentrations of the reactants also raised to a power represented by the coefficients. Thus we have for the reaction

$$H_2O \rightleftarrows H^+ + OH^-$$

$$\text{(1)} \qquad \frac{[H^+][OH^-]}{[H_2O]} = K_e$$

where K_e is known as the equilibrium constant. Since the concentration of water is constant in any aqueous solution, equation (1) may be written

$$\text{(2)} \qquad [H^+][OH^-] = K_e[H_2O] = K_w$$

where K_w is the ionization product for water. Its value changes with a change in temperature; at 25° it has a value of 10^{-14}, and at any constant temperature its value remains the same whether we are dealing with pure water or with an aqueous solution of an acid, a base or a salt. It follows then that if the concentration of either ion is known that of the other is calculable simply by dividing K_w by the known concentration. Obviously the acidity or basicity of any solution may be expressed in terms of either the hydrogen or the hydroxyl ion. For example, a solution of a strong

monobasic acid which is 0.1 *M* will yield a concentration of hydrogen ion of 0.1 *M*; the concentration of the hydroxyl ion of necessity must be $10^{-14}/10^{-1} = 10^{-13}$. It is logical, even if not customary, to state that such an acid solution is 10^{-13} molar with respect to hydroxyl ion.

From equation (2) it also follows that a neutral solution, being one in which neither the hydrogen nor the hydroxyl ion is in excess, is a solution in which

$$[H^+] = [OH^-] = \sqrt{10^{-14}} = 10^{-7} \tag{3}$$

and, *strictly speaking*, neutralization should be defined as a process in which the resulting concentrations of these two ions have a value of 10^{-7}. It must be remembered, though, that in analyses the object of an acid-base titration is to bring together chemically equivalent quantities of the reactants and not, *necessarily*, to bring about strict neutrality.

Instead of expressing the acidity or basicity of a solution in terms of $[H^+]$ or of $[OH^-]$ it is customary and more convenient to use a mathematical function[2] of the former known as the pH. The pH is the negative logarithm of the concentration of the hydrogen ion, or

$$pH = -\log [H^+]$$

Since acidic solutions used in analytical chemistry are seldom greater than 1 *N* the pH of the solutions usually will be represented by small, positive numbers rather than by the small, fractional numbers which result if the hydrogen ion concentration itself is given. This is evident from Table 7.

Table 7

THE RELATION BETWEEN HYDROGEN ION CONCENTRATION, HYDROXYL ION CONCENTRATION AND pH FOR CERTAIN SOLUTIONS

Solution	$[H^+]$	$[OH^-]$	pH
1 *N* HCl	10^{0}	10^{-14}	0
0.1 *N* HCl	10^{-1}	10^{-13}	1
0.01 *N* HCl	10^{-2}	10^{-12}	2
0.000001 *N* HCl	10^{-6}	10^{-8}	6
Pure water	10^{-7}	10^{-7}	7
0.000001 *N* NaOH	10^{-8}	10^{-6}	8
0.01 *N* NaOH	10^{-12}	10^{-2}	12
0.1 *N* NaOH	10^{-13}	10^{-1}	13
1 *N* NaOH	10^{-14}	10^{0}	14

A solution having a pH less than 7.0 is acidic while one having a pH above 7.0 is basic. The calculation of the pH when the concentration of

[2] Sörensen, *Biochem. Z.*, **21**, 131 (1909).

the hydrogen ion is known is quite simple. When the normality of the solution is an integral power of 10 the pH results at once; it obviously is the exponent of $[H^+]$ with the sign changed as is seen in Table 7. The calculation is never difficult, however, even if sometimes more involved, as may be seen in the following illustrations involving strong acids and bases.

1. *Problem.* What is the pH of 0.15 *N* solution of HCl?
   Solution. Since the acid is completely dissociated

$$[H^+] = 0.15 = 1.5 \times 10^{-1}$$
$$pH = -\log 1.5 \times 10^{-1}$$
$$pH = 0.82$$

2. *Problem.* What is the pH of a 0.15 *N* solution of H_2SO_4?

   Solution.
$$[H^+] = 0.15 = 1.5 \times 10^{-1}$$
$$pH = -\log 1.5 \times 10^{-1}$$
$$pH = 0.82$$

3. *Problem.* What is the pH of a 0.15 *M* solution of H_2SO_4?
   Solution. Considering the acid as completely ionized and remembering that one molecule of H_2SO_4 yields two hydrogen ions

$$[H^+] = 2 \times 0.15 = 3.0 \times 10^{-1}$$
$$pH = -\log 3.0 \times 10^{-1}$$
$$pH = 0.52$$

4. *Problem.* What is the pH of a 0.0050 *N* solution of NaOH?
   Solution. Since the base is completely dissociated

$$[OH^-] = 0.0050 = 5.0 \times 10^{-3}$$

By equation (2),

$$[H^+] = \frac{10^{-14}}{5.0 \times 10^{-3}} = \frac{10 \times 10^{15}}{5.0 \times 10^{-3}} = 2.0 \times 10^{-12}$$
$$pH = -\log 2.0 \times 10^{12}$$
$$pH = 11.7$$

Hydrogen Ion Concentration of Weak Acids and Bases

Two factors govern the hydrogen ion concentration established by solutions of weak acids and bases—namely, the concentration and the degree of ionization. One should recognize at once the difference between what may be called the *analytical* concentration of the electrolytic solute, and the ionic concentration which the solute establishes through partial dissociation. The analytical concentration represents the total concentration, molecular and ionic, whereas the latter designates only that part which is in the form of ions.

Consider a solution of a weak monobasic acid, HA, with a concentra-

tion of C moles per liter. Since it is partly ionized, the molecular HA is in equilibrium with the ions H^+ and A^-

$$HA \rightleftarrows H^+ + A^-$$

Applying the Law of Mass action we have

$$\frac{[H^+][A^-]}{[HA]} = K_a \tag{4}$$

where K_a is the ionization constant for the acid and is a constant for a given temperature. In a pure solution of the acid evidently there are equal numbers of H^+ ions and A^- ions; therefore

$$[H^+] = [A^-]$$

The concentration of the unionized acid [HA] is equal to the total concentration, C, less that which has dissociated, or

$$[HA] = C - [H^+]$$

Substitution in equation (4) yields

$$\frac{[H^+]^2}{C - [H^+]} = K_a \tag{5}$$

Since, however, for weak acids, the value of $[H^+]$ is very small compared to C, equation (5) may be written as a close approximation

$$\frac{[H^+]^2}{C} \cong K_a$$

or

$$[H^+] \cong \sqrt{CK_a} \tag{6}$$

Equation (6) may be employed for weak acids except for very great dilutions. (At infinite dilution the dissociation is complete even for weak acids.)

Problem. What is the pH of a 0.020 *N* solution of acetic acid? $K_a = 1.8 \times 10^{-5}$.

Solution.

$$[H^+] = \sqrt{(2.0 \times 10^{-2})(1.8 \times 10^{-5})}$$
$$= \sqrt{3.6 \times 10^{-7}} = \sqrt{36 \times 10^{-8}}$$
$$[H^+] = 6.0 \times 10^{-4}$$
$$pH = -\log 6.0 \times 10^{-4}$$
$$pH = 3.2$$

In the case of a weak dibasic acid, H_2A, the ionization takes place in two steps

$$H_2A \rightleftarrows H^+ + HA^-$$
$$HA^- \rightleftarrows H^+ + A^-$$

but in the majority of cases the second ionization step takes place to a comparatively negligible extent so that the hydrogen ion concentration may be calculated by equation (6), using K_{a_1}, the *first* ionization constant, for the dissociation of the dibasic acid. That is,

$$[H^+] \cong \sqrt{CK_{a_1}} \tag{6a}$$

Now consider a solution of a weak base, BOH, of a concentration of C moles per liter. Its ionization is represented by the reversible equation

$$BOH \rightleftarrows B^+ + OH^-$$

In a manner exactly analogous to the derivation of the value of $[H^+]$ established by a weak acid, equation (6), it may be shown that

$$[OH^-] \cong \sqrt{CK_b}$$

But from equation (2)

$$[OH^-] = K_w/[H^+]$$

Therefore

$$\frac{K_w}{[H^+]} \cong \sqrt{CK_b}$$

or

$$[H^+] \cong \frac{K_w}{\sqrt{CK_b}} \tag{7}$$

Problem. What is the pH of a 0.020 *N* solution of NH_4OH? $K_b = 1.8 \times 10^{-5}$.

Solution.

$$[H^+] = \frac{10^{-14}}{\sqrt{(2.0 \times 10^{-2})(1.8 \times 10^{-5})}}$$

$$[H^+] = 1.7 \times 10^{-11}$$

$$pH = -\log 1.7 \times 10^{-11}$$

$$pH = 10.8$$

Note that this is above the point of neutrality, 7.0, to the same extent as the pH for the acetic acid solution was found to be below 7.0. This is true, of course, because the two factors affecting the pH—namely, concentration and ionization constants—were the same in both cases.

Hydrolysis of Salts

By hydrolysis is meant the reaction of a salt and water to form an acid and a base. The nature of the solution resulting from hydrolysis will differ depending upon the kind of salt undergoing the hydrolysis. Therefore, let us take up the subject from the standpoint of the several types of salts: salts of strong acids and strong bases, salts of weak acids and strong bases, and the like. The behavior of salts when they hydrolyze bears importantly upon acid-base titrations, for when an acid and a base are titrated there should be present at the end point only salt; the pH at the end point

therefore is that which is established by the salt formed. An indicator must be chosen for each titration which will notify the analyst that chemically equivalent quantities of acid and base have been brought together. Thus if one knows the pH value which the resulting salt yields, one may select an indicator which changes color at this same pH value, or close to it, and therefore may stop the titration at the proper point. We shall now proceed to see how the pH of aqueous salt solutions is calculated.

Salts of Strong Acids and Strong Bases. A salt of a strong acid and a strong base, like sodium chloride, does not undergo hydrolysis since both the acid and the base are completely ionized. Such a solution has a pH of 7.0.

Salts of Weak Acids and Strong Bases. Consider the sodium salt of the weak acid, HA. It will react with water,

$$Na^+ + A^- + H_2O \rightleftarrows Na^+ + HA + OH^-$$

or essentially

$$A^- + H_2O \rightleftarrows HA + OH^- \tag{8}$$

The mass law expression for this reaction will lead to the pH of the salt solution.

$$\frac{[HA][OH^-]}{[A^-][H_2O]} = K$$

But since the value of $[H_2O]$ remains practically constant

$$\frac{[HA][OH^-]}{[A^-]} = K_h \tag{9}$$

where K_h is the hydrolysis constant. Knowing that

$$[H^+][OH^-] = K_w$$

and that

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

we obtain by dividing the former by the latter

$$\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} \tag{10}$$

Evidently then, since K_h of equation (9) and K_w/K_a of equation (10) are equal to the same thing, it follows that

$$\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} = K_h \tag{11}$$

From equation (8) it is seen that for each OH^- ion there is one molecule of HA. Therefore we may replace [HA] in equation (11) with $[OH^-]$ and obtain

$$\frac{[OH^-]^2}{[A^-]} = \frac{K_w}{K_a}$$

Assuming complete dissociation for the salt, NaA, so that $[A^-] = C - [OH^-]$, where C is the concentration of the salt in moles per liter, and remembering that $[OH^-]$ is much smaller than C, we have

$$\frac{[OH^-]^2}{C} \cong \frac{K_w}{K_a}$$

or

$$[OH^-] \cong \sqrt{\frac{K_w C}{K_a}}$$

Since from equation (2)

$$[OH^-] = K_w/[H^+]$$

then

$$\frac{K_w}{[H^+]} \cong \sqrt{\frac{K_w C}{K_a}}$$

from which

$$[H^+] \cong \sqrt{\frac{K_w K_a}{C}} \tag{12}$$

Problem. What is the pH of a 0.025 *N* solution of $NaC_2H_3O_2$?

Solution.

$$[H^+] = \sqrt{\frac{(10^{-14})(1.8 \times 10^{-5})}{2.5 \times 10^{-2}}}$$

$$= \sqrt{7.2 \times 10^{-18}}$$

$$[H^+] = 2.7 \times 10^{-9}$$

$$pH = -\log 2.7 \times 10^{-9}$$

$$pH = 8.6$$

Salts of Weak Bases and Strong Acids. The corresponding case of the pH of a solution of a salt of a weak base and a strong acid is even simpler. Consider the chloride salt of the weak base, BOH. It will react with water

$$B^+ + Cl^- + H_2O \rightleftarrows BOH + H^+ + Cl^-$$

or essentially

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

From the Law of Mass Action and assuming the concentration of water to be constant, we obtain

$$\frac{[BOH][H^+]}{[B^+]} = K_h = \frac{K_w}{K_b} \tag{13}$$

K_b being the ionization constant of the weak base. Now $[BOH] = [H^+]$ and $[B^+] \cong C$, where C is the concentration of the salt, and substituting these values in equation (13)

$$\frac{[H^+]^2}{C} \cong \frac{K_w}{K_b}$$

from which

$$[H^+] \cong \sqrt{\frac{K_w C}{K_b}} \tag{14}$$

Problem. What is the pH of a 0.025 *N* solution of NH_4Cl?

Solution.

$$[H^+] = \sqrt{\frac{(10^{-14})(2.5 \times 10^{-2})}{1.8 \times 10^{-5}}}$$
$$= \sqrt{1.4 \times 10^{-11}}$$
$$[H^+] = 3.7 \times 10^{-6}$$
$$pH = -\log 3.7 \times 10^{-6}$$
$$pH = 5.4$$

Salts of Weak Acids and Weak Bases. In the two former cases the pH established by the salt was found to be governed by the concentration C of the salt and by the ionization constant K_a or K_b. In the present case we shall see that the ionization constants of both the weak acid and weak base (from which the salt is regarded as being formed) influence the pH of the salt solution. The salt of the weak acid, HA, and the weak base, BOH, may be used to illustrate this type of reaction. The ions from this salt, BA, will react with water as follows

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

and

$$A^- + H_2O \rightleftarrows HA + OH^-,$$

from which it follows that

$$\frac{[BOH][H^+]}{[B^+]} = K_{h_1} = \frac{K_w}{K_b} \tag{15}$$

and

$$\frac{[HA][OH^-]}{[A^-]} = K_{h_2} = \frac{K_w}{K_a} \tag{16}$$

Of course, simultaneously, the following also must be satisfied:

$$[H^+][OH^-] = K_w$$

Dividing the product of the two former by the last yields

$$\frac{[BOH][HA]}{[B^+][A^-]} = \frac{K_{h_1}K_{h_2}}{K_w} = \frac{K_w}{K_aK_b} \tag{17}$$

Assuming complete ionization of the salt and that the weak acid and the weak base are ionized to about the same degree, it follows that

$$[HA] \cong [BOH]$$

and

$$[B^+] \cong [A^-] \cong C$$

Substituting these values in equation (17)

$$\frac{[HA]^2}{C^2} \cong \frac{K_w}{K_a K_b}$$

or

$$[HA] \cong C\sqrt{\frac{K_w}{K_a K_b}}$$

Substitution of this value of [HA] (and also C for $[A^-]$) in the mass law expression for the ionization of the weak acid, HA, namely,

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

will yield the value of $[H^+]$, thus:

$$\frac{[H^+][C]}{C\sqrt{\frac{K_w}{K_a K_b}}} \cong K_a$$

or, solving for $[H^+]$,

(18)
$$[H^+] \cong K_a\sqrt{\frac{K_w}{K_a K_b}} \cong \sqrt{\frac{K_w K_a}{K_b}}$$

Note that the following conclusions may be drawn regarding the solution of a salt of a weak acid and a weak base. First, the pH is independent of the concentration of the solution. Second, from equation (17) it is obvious that the smaller the value of the product $K_a K_b$ the larger will be the value of $K_w/K_a K_b$ and thus the greater the extent of the hydrolysis. Third, from equation (18) it is evident that when the ratio of K_a/K_b exceeds unity (that is, when the ionization constant of the weak acid is greater than that of the weak base), the solution of the salt will give an acidic reaction; the pH will be less than 7.0. Conversely, if the ratio K_a/K_b is less than unity the solution of the salt will give a basic reaction; the pH will be greater than 7.0. A salt like ammonium acetate will give a neutral reaction since the values of K_a and K_b for acetic acid and ammonium hydroxide are almost identical, 1.8×10^{-5}.

Problem. What is the pH of a solution of $NH_4C_2H_3O_2$?

Solution.

$$[H^+] = \sqrt{\frac{(10^{-14})(1.8 \times 10^{-5})}{1.8 \times 10^{-5}}}$$

$$[H^+] = 10^{-7}$$

$$pH = -\log 10^{-7}$$

$$pH = 7.0$$

Problem. What is the pH of a solution of $HCOONH_4$? $K_a = 1.8 \times 10^{-4}$; $K_b = 1.8 \times 10^{-5}$.

Solution.

$$[H^+] = \sqrt{\frac{(10^{-14})(1.8 \times 10^{-4})}{1.8 \times 10^{-5}}}$$

$$[H^+] = 3.2 \times 10^{-7}$$

$$pH = -\log 3.2 \times 10^{-7}$$

$$pH = 6.5$$

Acid-Salts. Consider the primary sodium salt of the dibasic acid H_2A. In solution it ionizes according to the equation

$$NaHA \rightarrow Na^+ + HA^-$$

But the anion HA^- itself will ionize to some extent:

(19) $$HA^- \rightleftarrows H^+ + A^=$$

and also will hydrolyze:

(20) $$HA^- + H_2O \rightleftarrows H_2A + OH^-$$

The reaction of equation (19) yields H^+ ions while that of (20) yields OH^- ions. If we assume, as is true in most cases, that these two reactions go forward to about the same extent, then

(21) $$[A^=] \cong [H_2A]$$

The mass law expressions for equations (19) and (20) are

$$\frac{[H^+][A^=]}{[HA^-]} = K_{a_2}$$

and

$$\frac{[H_2A][OH^-]}{[HA^-]} = K_h = \frac{K_w}{K_{a_1}}$$

and dividing the former by the latter

(22) $$\frac{[H^+][A^=]}{[H_2A][OH^-]} = \frac{K_{a_1}K_{a_2}}{K_w}$$

From equation (21) we may substitute $[H_2A]$ for $[A^=]$ and from equation (2) we may replace $[OH^-]$ by $K_w/[H^+]$. Making these substitutions in equation (22) and solving for $[H^+]$ gives

(23) $$[H^+] \cong \sqrt{K_{a_1}K_{a_2}}$$

This approximation may be employed only if K_{a_1} and K_{a_2} are small compared with C, the concentration of the salt; otherwise equation (21) is invalid and thus also equation (23).

Problem. What is the pH of a solution of $NaHCO_3$ of moderate concentration? $K_{a_1} = 3.0 \times 10^{-7}$; $K_{a_2} = 6.0 \times 10^{-11}$.

Solution.

$$[H^+] = \sqrt{(3.0 \times 10^{-7})(6.0 \times 10^{-11})}$$
$$[H^+] = 4.2 \times 10^{-9}$$
$$pH = -\log 4.2 \times 10^{-9}$$
$$pH = 8.4$$

Normal Salts of Dibasic Acids. The equation for the hydrogen ion concentration of a solution of the normal, or secondary, salt of a dibasic acid is derived in a manner analogous to that of equation (12) except that K_a is replaced by K_{a_2}, the secondary ionization constant. That is,

$$[H^+] \cong \sqrt{\frac{K_w K_{a_2}}{C}} \tag{24}$$

Problem. What is the pH of a 0.0100 *M* solution of Na_2CO_3? $K_{a_2} = 6.0 \times 10^{-11}$.

Solution.

$$[H^+] = \sqrt{\frac{(10^{-14})(6.0 \times 10^{-11})}{10^{-2}}}$$
$$[H^+] = 7.7 \times 10^{-12}$$
$$pH = -\log 7.7 \times 10^{-12}$$
$$pH = 11.1$$

Buffer Solutions. A solution containing both a weak acid and a salt of that acid, or one containing both a weak base and a salt of that base, will establish a pH which is not greatly affected by the addition of moderate amounts of even strong acids or bases. Such solutions are called *buffer* solutions. Often in quantitative analyses provision must be made to keep the pH of a solution fairly constant. The use of a buffer is generally employed for this purpose. The particular pH which a certain buffer will give depends upon two factors: the concentrations of the electrolytes employed and the ionization constant of the weak acid (or weak base). Therefore, within reasonable limits, a buffer of any desired pH may be prepared.

The hydrogen ion concentration of a buffer made with a weak acid and one of its salts may be calculated from an equation developed as follows. The mass law expression for a weak acid, HA, and its ions is

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

Therefore

$$[H^+] = \frac{[HA]}{[A^-]} \cdot K_a$$

In the presence of one of its salts the value of $[A^-]$ will be approximately that furnished by the salt alone, or C, since the acid is weak and the salt is assumed completely ionized. Thus the above equation becomes

$$[H^+] \cong \frac{[HA]}{C} \cdot K_a \tag{25}$$

A buffer made up of a weak base and one of its salts will set up a hydroxyl ion concentration found, by a derivation similar to that of

equation (25), to be

$$[OH^-] \cong \frac{[BOH]}{C} \cdot K_b$$

or, substituting $K_w/[H^+]$ for $[OH^-]$ and solving for $[H^+]$,

$$[H^+] \cong \frac{K_w C}{[BOH]K_b} \tag{26}$$

Equations (25) and (26) therefore may be used to compute the value of $[H^+]$, and thus the pH, of all such buffer solutions. Note that in both cases the value of $[H^+]$ is equal to a constant (K_a for acid buffers and K_w/K_b for basic buffers) multiplied by the ratio of the concentrations of the acid and the salt (or of the salt and the base). Since the acid (or the base) and its salt are in the same solution, the volume of the solution has no effect upon the hydrogen ion concentration, unless, indeed, the dilution be extremely great.

The reason that a buffer solution resists changes in pH lies in the fact that no matter whether an acid or a base is added to the buffer a reaction takes place to prevent most of the newly added H^+ ion or OH^- ion from remaining as such. An acid buffer may be used to illustrate the point. If acetic acid and sodium acetate make up the buffer, the solution contains acetic acid molecules and hydrogen, sodium, hydroxyl and acetate ions. If hydrochloric acid is now added the hydrogen ions from it largely combine with the acetate ions to form more acetic acid molecules, and the value of $[H^+]$ varies only slightly. On the other hand, if sodium hydroxide is added to the buffer the hydroxyl ions from it largely combine with hydrogen ions to form water, and again the value of $[H^+]$ is changed very little. A buffer, to be most effective—that is, to resist changes in hydrogen ion concentration when *either* acid *or* base is added—should be made up in an equimolar ratio of weak acid (or weak base) and salt, for then potentially there will be present sufficient concentrations of ions to take care of either hydrogen ion or hydroxyl ion from the newly added acid or base. This refers, of course, to the *capacity* of the buffer to offset changes in pH. The particular pH which a given buffer sets up and approximately maintains is governed, let it be repeated, by the magnitude of the ionization constant involved and by the concentrations of the acid (or base) and its salt.

Suppose that a buffer having a pH of about 5 is wanted. A weak acid having an ionization constant of around 10^{-5} may be employed. From equation (25) it follows that equimolar quantities of acetic acid and sodium acetate in solution will give a pH of 4.74 for

$$[H^+] = 1/1(1.8 \times 10^{-5})$$
$$pH = -\log 1.8 \times 10^{-5}$$
$$pH = 4.74$$

If a buffer of exactly pH = 5.0 is desired, acetic acid and sodium acetate may still be used but not in equimolar ratio. The proper ratio in this case is calculated from equation (25). For a pH of 5.0 the value of $[H^+]$ is 10^{-5}. Therefore

$$10^{-5} = \frac{[HAc]}{C}(1.8 \times 10^{-5})$$

$$\frac{[HAc]}{C} = \frac{1}{1.8}$$

That is, if a solution is made up containing 1 mole of acetic acid to 1.8 moles of sodium acetate it will give a pH of 5.0.

To illustrate the power of buffers to resist variation in pH we may calculate the change brought about by adding either a strong acid or a strong base to an unbuffered solution on the one hand, and to a buffered solution on the other.

Suppose we have 100 ml. of pure water (or of any neutral unbuffered solution). The pH will be 7.0. If the water contained 5 ml. of exactly 0.1 *M* HCl the resulting solution obviously would be 0.0050 *M* with respect to HCl and

$$[H^+] = 5.0 \times 10^{-3}$$
$$pH = 2.3 \text{ and } \Delta pH = 4.7$$

If, instead of HCl, the water contained 5 ml. of exactly 0.1 *M* NaOH, then

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{5.0 \times 10^{-3}}$$
$$[H^+] = 2.0 \times 10^{-12}$$
$$pH = 11.7 \text{ and again } \Delta pH = 4.7$$

Suppose, on the other hand, we make up a buffer by adding together exactly 50 ml. of 0.1 *M* $HC_2H_3O_2$ and 50 ml. of 0.1 *M* $NaC_2H_3O_2$. As has been pointed out already, this buffer will have a pH of 4.74, since from equation (25)

$$[H^+] = \frac{0.0500}{0.0500}(1.8 \times 10^{-5})$$
$$pH = 4.74$$

If the 100 ml. of buffer also contained 5 ml. of 0.1 *M* HCl the hydrogen ions of the hydrochloric acid would combine almost completely with acetate ions of the buffer, thus bringing the value of [HAc] to 0.0550 and simultaneously decreasing the value of C to 0.0450. Therefore

$$[H^+] = \frac{0.0550}{0.0450}(1.8 \times 10^{-5})$$
$$[H^+] = 2.20 \times 10^{-5}$$
$$pH = 4.66 \text{ and } \Delta pH = 0.08$$

If, instead of hydrochloric acid, the buffer contained 5 ml. of 0.1 *M* NaOH, the hydroxyl ions would combine almost completely with hydrogen ions of the buffer, thus decreasing the value of [HAc] to 0.0450 and simultaneously increasing the value of C to 0.0550. Therefore

$$[H^+] = \frac{0.0450}{0.0550}(1.8 \times 10^{-5})$$

$$[H^+] = 1.47 \times 10^{-5}$$

$$pH = 4.83 \text{ and } \Delta pH = 0.09$$

Thus, whereas the addition of 5 ml. of 0.1 *M* solution of strong acid or base to 100 ml. of unbuffered solution changed the pH by 4.7 pH units, the same treatment of the acetic acid–acetate buffer changed the pH by less than 0.1 pH unit. That is to say that the effect of the acid or base proves to be, in the case at hand, about 50 times as great upon the unbuffered solution as upon the buffered solution ($4.7/ < 0.1 \cong 50$).

Indicators for Acid-Base Titrations

Acid-base indicators are organic dyes which exhibit the characteristic of changing from one color to another, or becoming colorless, when the pH of the solution in which they are dissolved is varied slightly. The particular pH value at which the change in color occurs is different for different indicators. Therefore an indicator, if properly chosen, may be employed to mark the end point for an acid-base titration, provided the pH established when chemically equivalent quantities of acid and base have been brought together is known. Indicators are usually weak organic acids or bases and their tinctorial power is so high that they may be used in very low concentration. The color which a given indicator assumes at any pH value may be ascertained by placing a few drops in each of a series of buffer solutions of definite and ascending pH values. Methyl orange indicator, for example, in an acidic solution with a pH of 1 shows a pink color. In a solution of a somewhat higher pH the methyl orange begins to show an orange color. The orange tint first becomes apparent at a pH of about 3.1. After the pink color has completely disappeared and is replaced by pure orange the pH will be found to have a value of around 4.4. The pH interval, 3.1 to 4.4, during which the color was changing from pink to orange, is called the *range* of the indicator. Within the *range* of the indicator there is a pH value at which a distinct and fairly abrupt change of hue takes place; this happens ordinarily when the tint is about midway between the two extremes of color, and in the case of methyl orange at a pH of about 4.0. This is called the *transition* pH of the indicator.

Table 8 gives a few of the indicators commonly used in volumetric analysis and the pH at which the color change occurs.

Table 8

INDICATOR COLORS AND RANGES*

Indicator	pH *Range*	*Transition* pH	*Transition Color*	*Lower Range Color*	*Higher Range Color*
Bromphenol blue.....	3.0–4.6	3.6	green	yellow	blue
Methyl orange.....	3.1–4.4	4.0	orange	red	yellow
Methyl red.....	4.2–6.3	5.6	orange	red	yellow
Phenol red.....	6.8–8.4	7.0	orange	yellow	red
0 03 *M* Phenolphthalein...	8.3–10.0	8.4	pale pink	colorless	red
0 003 *M* Phenolphthalein..	9.2–10.0	9.3	pale pink	colorless	red
Thymolphthalein.....	9.4–10 5	9.5	pale blue	colorless	blue

*Data from W. M. Clark, *The Determination of Hydrogen Ions*, Williams & Wilkins Co., Baltimore, 1928.

The transition color of two-color indicators is somewhat a matter of individual opinion. One analyst may consistently carry his titrations to a slightly higher pH than another when using methyl orange, for example; but so long as he is consistent in obtaining the same tint of orange color every time, it is not important that the exact hue to which he titrates is slightly different from that obtained by another worker.

THEORY OF INDICATORS

Since the organic dyes used as indicators for acid-base titrations are either weak acids or weak bases the reaction for their ionization may be written

(27) $$HIn \rightleftarrows H^+ + In^-$$

and $$InOH \rightleftarrows In^+ + OH^-$$

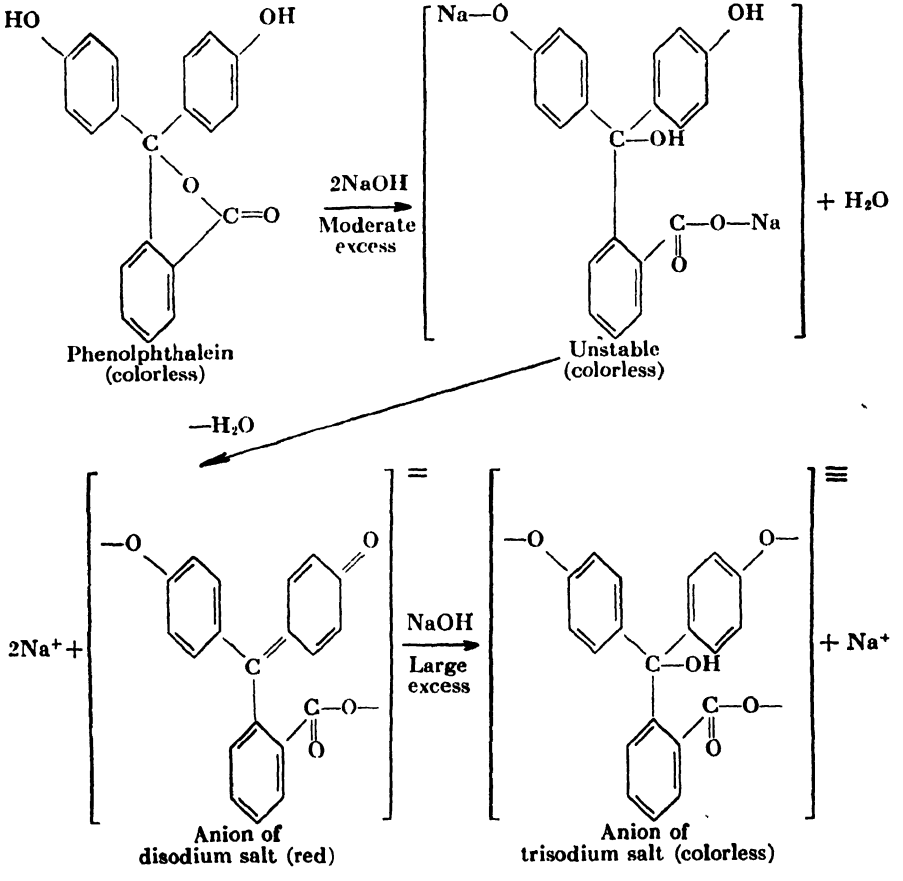
Consider the first, a weak acid indicator, as an example. Ostwald[3] suggested that such an indicator owes its color change to the fact that the molecule, HIn, is of one color (or colorless, as in the case of phenolphthalein) and the anion, In^-, is of another color. Therefore an acid indicator in an acidic environment should be, for all practical purposes, undissociated; that is, the ionic equilibrium should be shifted so far to the left (equation (27)) that practically none of the colored In^- ion remains in the solution. In a basic environment the indicator reacts with the base of the titration (after the acid of the titration has been satisfied) forming the salt—e.g., NaIn—which salt is highly ionized and therefore imparts the characteristic In^- color to the solution.

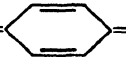
There is much evidence that the mechanism involved when indicators undergo a color change is not so simple as depicted above. The organic chemist long since has established through his elegant syntheses that color is associated with definite

[3] Ostwald, *Die wissenschaftlichen Grundlagen der analytiche Chemie*, W. Engelmann, Leipzig, 1894.

molecular structure. At least one of these color groups within the organic molecule is always present when color manifests itself; such groups are called chromophores. Reduced to its simplest argument it is thought that indicators change color, not because of ionization, *per se*, but because the ionization is accompanied by intramolecular rearrangement which either produces or eliminates a chromophoric group. This point of view may be illustrated with what is thought to take place in the case of phenolphthalein.

The quinoid chromophore, , is not present in the structure of the phenolphthalein molecule, and the molecule is colorless. In the presence of a small or a moderate amount of excess base, phenolphthalein is converted into an unstable intermediate which loses water to form the disodium salt. The anion of this salt does contain the chromophore and the red color appears. The fact that a large excess of base causes phenolphthalein to lose its red color is accounted for by the formation of the trisodium salt in which the quinoid structure has been lost. These relationships are shown in the following structural formulas.



Only the anion of the disodium salt of phenolphthalein contains the chromophoric function,  ; therefore it alone gives the red color.

The interpretation given by Ostwald to account for color changes in indicators is obviously simpler than the chromophoric theory and, while the latter is doubtless nearer the truth, we may employ the more elementary approach in studying the ionic equilibrium involved. Applying the mass law to equation (27) we obtain

$$\frac{[H^+][In^-]}{[HIn]} = K_{In} \tag{28}$$

or

$$[H^+] = \frac{[HIn]}{[In^-]} \cdot K_{In} \tag{29}$$

where K_{In} is the indicator constant. The intensity of color is proportional to the concentration of the colored unit, so that for a two-color indicator equation (29) may be written

$$[H^+] = k \cdot \frac{\text{Intensity of Color I}}{\text{Intensity of Color II}} \cdot K_{In} \tag{30}$$

from which it follows that the color actually seen depends only upon the hydrogen ion concentration. Now the eye has its limits in recognizing a given color when two colors are present. If, as in the case of methyl orange, the colors are red and yellow, the eye is unable to distinguish between pure red color and that resulting from a mixture of 95 per cent red and 5 per cent yellow. As a matter of fact the uncertainty generally exists until the ratio of [HIn] to [In^-] is about 10. In a solution in which the ratio is greater than 10 the eye gets the impression that the color is that of the pure "acid" hue; likewise, if the ratio is less than 0.1 the color appears to be that of the pure "basic" tint. The range of any indicator is that pH span for which the above-mentioned ratio is between 10:1 and 1:10. Between these ratios the eye registers an intermediate color. It follows that an indicator changes its color abruptly only if the pH suddenly varies over the range of the indicator. If we substitute the values 10 and 0.1 for [HIn]/[In] in equation (29) we obtain $[H^+] = 10K_{In}$ and $[H^+] = 0.1K_{In}$, or in terms of pH

$$pH = pK_{In} \pm 1$$

where $pK_{In} = -\log K_{In}$. Thus the pH range necessary for a change from one color to the other for a given indicator will be

$$\Delta pH = (pK_{In} + 1) - (pK_{In} - 1) = 2$$

The above calculation of ΔpH is based upon the assumption that the one colored form must be of a concentration 10 times the other before the eye registers the effect of a pure color. The confirmation of the validity of this assumption may be seen in Table 8 where the range for typical indicators is found to be about two pH units. Finally, it should be noted that if, during a titration, the concentration of the reagent added from the buret

is such that one drop will cause a change of two pH units in the solution being titrated, a sharp end point will result. If, however, two or three drops must be added to produce a change in pH of two units, the end point will be gradual and the titration less satisfactory.

Mixed Indicators. It is sometimes possible to secure a sharper and a more pronounced color change by using together two indicators or one indicator and a dye. For example,[4] instead of methyl orange, one may use a solution of 1 g. of methyl orange and 2.5 g. of indigo carmine per liter of water. This gives a gray color at a pH of 4.0, but is violet below 4.0 and green above 4.0. Again 0.7 g. of methylene green and 0.3 g. of phenolphthalein in a liter of solution gives a mixed indicator which is light blue at a pH of 8.8 and is respectively green and violet immediately below and above 8.8.

Choice of Proper Indicator

It has already been stated that the object of any titration is to bring together chemically equivalent quantities of reactants. Furthermore, we have seen that when this is done in the case of an acid and a base the resulting salt solution may have a pH above, below or equal to 7.0 depending on the particular titration. We know also that different indicators have different pH ranges. From these facts it should be clear that the proper indicator for a given titration is *that indicator having a* pH *range which includes the* pH *established by the salt formed as a result of the acid-base titration.* Any indicator meeting this requirement will be suitable provided that its pH range is spanned upon the addition of one or two drops of reagent from the buret. The pH which is established by the salt resulting from the titration is calculated, as already set forth, from equation (12), (14), (18), (23) or (24). This done, the proper indicator may be chosen from Table 8 or from more extensive tables found elsewhere.

Titration Curves

The manner in which the pH varies during the course of a titration is best displayed by plotting a graph with the pH values as the ordinate and the volume of reagent added from the buret as the abscissa. Such curves may be constructed from pH measurements obtained experimentally, or the data for the graphs may be calculated. The calculated curves are in general a close approximation of those plotted from experimental data; the fact that they are approximations is understood when it is remembered that most of the equations already developed for computing pH values involve simplifying assumptions. In deriving these equations the point at which the approximation symbol, $\cong$, first appears denotes the introduction of the slight departure from strict equality.

[4] See also Kolthoff and Stenger, *Volumetric Analysis*, Vol. II, Interscience Publishers, New York, 1947.

It must be pointed out, furthermore, that we have defined pH as equal to $-\log [H^+]$ whereas as a matter of fact $pH = -\log (H^+)$ where (H^+) is the *activity* of the hydrogen ion. In general, calculations which are involved in ionic equilibria are not quite in accord with experimental observations when the concentrations of ions are employed. Deviations become more pronounced as the solutions become more concentrated, and especially in solutions containing foreign ions. Debye and Hückel[5] have shown the relationship between concentration and activity based upon the assumption that solutions of strong electrolytes are totally ionized and that there exists an attraction between ions due to the electrical charges which they bear. The factor by which the concentration must be multiplied in order that such calculations as are involved in solubility products, pH, etc., may tally precisely with experimental results, is called the *activity coefficient.* The coefficient thus is a factor which gives the fraction of the concentration of an ion which is effective in the equilibrium under consideration; that is, it measures the *effective* ionization. At infinite dilution the activity coefficient becomes unity but at moderate concentrations the coefficient for a given ion in a given solution will be significantly less than unity. In regard to pH with which we are at present concerned the error caused by using $[H^+]$ instead of (H^+) usually amounts to less than 0.2 pH unit.

The calculation of titration curves becomes a simple matter when it is borne in mind that there are just four types of points to be computed. They are: (1) the pH at the beginning, before any reagent has been added from the buret; (2) the pH for points after additions from the buret but before the stoichiometric point; (3) the pH at the stoichiometric point; and (4) the pH for points past the stoichiometric point.

The methods of calculating these four types of points are somewhat different for the titration of a strong acid and strong base from the methods used when one of the reactants is weak. We now may proceed to illustrate the calculations for a few typical titrations.

Titration of a Strong Acid by a Strong Base. Consider the titration of 30 ml. of 0.1 *N* HCl by 0.1 *N* NaOH. Suppose that first the acid is diluted to a total volume of 100 ml. As the titration proceeds the total volume, of course, increases. The calculated values for the pH at various stages of the titration are given in Table 9. These should be checked by the student. The calculations of four typical points are given below.[6]

1. Before the addition of any base the solution consists only of hydrochloric acid, completely dissociated. The 0.1 *N* HCl (= 0.1 *M*) was diluted to 100 ml., therefore

$$[H^+] = \frac{30(0.1)}{100} = 0.0300 = 3.00 \times 10^{-2}$$

$$pH = -\log 3.00 \times 10^{-2} = 1.52$$

[5] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). See also Clark, *The Determination of Hydrogen Ions*, Williams and Wilkins Co., Baltimore, 1928, Chap. XXV; Briscoe, *General Chemistry for Colleges*, Houghton Mifflin Co., New York, 1943.

[6] In the following calculations it will be assumed that volumes are accurate to 0.01 ml. and concentrations to 0.0001 *M* so that the pH may be calculated with a precision of 1 part per 1000 if desired.

Table 9

TITRATION OF 0.1 *N* HCl BY 0.1 *N* NaOH. 30 ML. OF 0.1 *N* HCl DILUTED TO 100 ML. CALCULATED VALUES OF pH

Base Added in ml.	[H+]	pH
0.00	3.00×10^{-2}	1.52
1.00	2.87×10^{-2}	1.54
5.00	2.38×10^{-2}	1.62
10.00	1.82×10^{-2}	1.74
15.00	1.30×10^{-2}	1.88
20.00	8.33×10^{-3}	2.08
25.00	4.00×10^{-3}	2.40
29.00	7.76×10^{-4}	3.11
29.50	3.86×10^{-4}	3.41
29.80	1.54×10^{-4}	3.81
29 90	7.70×10^{-5}	4.11
29.95	3.85×10^{-5}	4.41
29 98	1.54×10^{-5}	4.81
30 00	1.00×10^{-7}	7.00
30.05	2.60×10^{-10}	9 58
30.10	1.30×10^{-10}	9.89
31 00	1.31×10^{-11}	10.88
35 00	2.70×10^{-12}	11.56
40.00	1.40×10^{-12}	11.85

2. After the addition of 20 ml. of base the solution may be thought of as containing 10 ml. of 0.1 *N* free acid plus 20 ml. of 0.1 *N* salt, diluted to a total volume of 120 ml. The salt does not appreciably affect the ionization of the HCl, therefore

$$[H^+] = \frac{10(0.1)}{120} = 8.33 \times 10^{-3}$$

$$pH = -\log 8.33 \times 10^{-3} = 2.08$$

3. At the stoichiometric point the solution contains only NaCl. This is a salt of a strong acid and a strong base and therefore does not hydrolyze; thus the pH is 7.00.

4. When excess base has been added the solution contains salt and excess hydroxyl ion. The salt has no great effect upon the concentration of hydroxyl ion which therefore depends upon the quantity of base added. For example, when 40 ml. of NaOH has been added we may regard the solution as containing salt and 10 ml. of 0.1 *N* free base diluted to a total of 140 ml. Therefore

$$[OH^-] = \frac{10(0.1)}{140} = 7.14 \times 10^{-3}$$

$$pH = 11.85$$

The data of Table 9 are plotted as a solid curve in Fig. 20. The shaded areas represent the range of the two indicators, phenolphthalein and methyl orange, as taken from Table 8. It is clear that because the steep portion of the curve extends over a long range in pH either phenolphthalein or methyl orange may be used as the indicator. Theoretically if phenolphthalein were used the end point would come when about 30.03 ml. of base have been added, for the pH would then be high enough to come within the color range of the indicator. On the other hand, if methyl orange were used the end point theoretically would come at about 29.95 ml. of base (if the titration be carried to pure yellow), for then the pH is 4.41 which is just to the higher side of the range of this indicator. The difference in using the two indicators should be about 0.1 ml. of base; in actual practice if 0.1 *N* solutions are used the difference found by most analysts amounts to about 0.15 ml. of base.

Obviously in secondary standardizations of strong acids against strong bases two values for the normality of a solution may be obtained, one from data secured by titrating when phenolphthalein is used and another when methyl orange is used. Suppose the values obtained are, respectively, 0.1035 *N* and 0.1029 *N*. The question sometimes is asked, which is the *correct* normality? The answer is, of course, that each is correct. When this solution is used in future analyses the value 0.1035 should be employed if phenolphthalein is the indicator and 0.1029 should be employed if methyl orange is the indicator. In other words, we only need to be consistent.

Fig. 20 also gives a second curve, for the titration of 0.001 *N* HCl by 0.001 *N* NaOH. By calculations exactly analogous to those from which the solid curve for 0.1 *N* solutions was plotted it may be seen that the pH after the addition of a given quantity of base is exactly 2.00 pH units higher for the dilute solutions until the stoichiometric point is reached; there the curves coincide. For volumes of base past the stoichiometric point the pH for the dilute solutions are 2.00 pH units lower than that for the 0.1 *N* solutions. This difference of 2.00 pH units must occur since the concentrations differ in the two cases by 10^2, the logarithm of which is 2.00. The more dilute the solutions the shorter is the steep portion of the titration curve. For 0.001 *N* solutions it is evident that neither phenolphthalein nor methyl orange could function as the indicator; instead an indicator with a color change taking place at a pH of between 6 and 8 is necessary. The kinds of difficulties encountered if one were to use either phenolphthalein or methyl orange for such a titration, if not already foreseen, will be clarified in the following section.

The flat portion of the curve in Fig. 20 from 0 to 25 ml. is not usually said to be due to buffer effect. It may be so called if a buffer solution were defined as any solution which resists change in pH. If, however, a buffer is defined as a solution of a weak acid (or base) and a salt of that acid (or base), then the titration of HCl by NaOH involves no buffer action. Rather, the reason for the flat portion of the curve is that here the solution is so strongly acidic that the small increments of base do not greatly vary the pH.

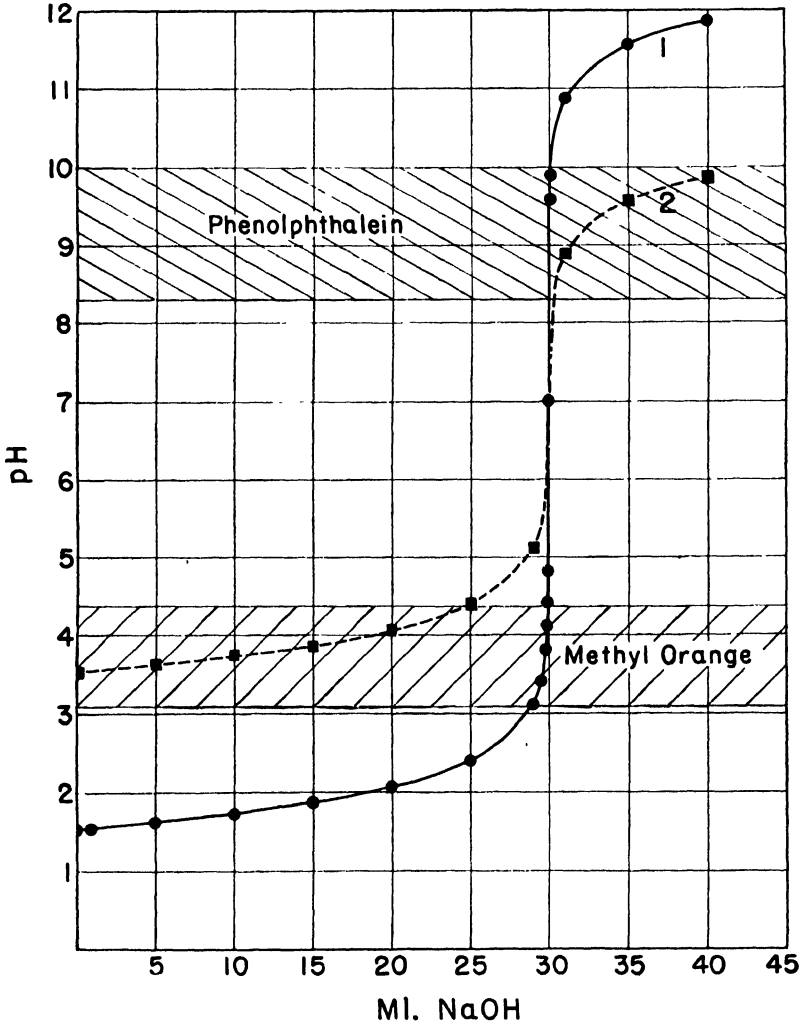


FIG. 20. Titration curves for HCl. Curve 1, 0.1 *N* HCl with 0.1 *N* NaOH; Curve 2, 0.001 *N* HCl with 0.001 *N* NaOH. Diluted from 30 ml. to 100 ml. before titrating.

Titration of a Weak Acid by a Strong Base. The construction of the titration curve for a weak acid and a strong base is somewhat more involved than that of the case first considered for three reasons: the acid, being weak, is incompletely dissociated; as the titration proceeds a salt is formed which represses the ionization of the acid; and the salt hydrolyzes. The first of these factors, incomplete dissociation of the acid, influences the calculation of the pH before any base has been added. The second affects calculations for points after addition of base but before the stoichiometric point is reached. The third influences the pH at, and immediately before and immediately after, the stoichiometric point. The titration of acetic acid by sodium hydroxide will illustrate this type of reaction. Table 10 lists pH values calculated for the titration of 30 ml. of 0.1 *N* HAc first diluted to 100 ml. and titrated with 0.1 *N* NaOH.

Table 10

TITRATION OF 0.1 *N* $HC_2H_3O_2$ BY 0.1 *N* NaOH. 30 ML. 0.1 *N* $HC_2H_3O_2$ DILUTED TO 100 ML. CALCULATED VALUES OF pH

Base Added in ml.	[H+] *by Equa. (25)*	pH *by Equa. (25)*	pH *by Equa. (25a)*
0.00	7.35×10^{-4}	3.13	
1.00	5.22×10^{-4}	(3.28)	3.43
2.00	2.52×10^{-4}	(3.60)	3.65
3.00	1.50×10^{-4}	(3.79)	3.82
5.00	9.00×10^{-5}	(4.05)	4.06
8.00	4.95×10^{-5}	4.30	4.30
10.00	3.60×10^{-5}	4.44	4.44
15.00	1.80×10^{-5}	4.74	4.74
20.00	9.00×10^{-6}	5.05	
25.00	3.60×10^{-6}	5.44	
29.00	6.21×10^{-7}	6.21	
29.50	3.05×10^{-7}	6.52	
29.80	1.21×10^{-7}	6.91	
29.90	6.02×10^{-8}	7.22	
29.95	3.01×10^{-8}	7.52	
30.00	2.80×10^{-9}	8.55	
30.05	2.60×10^{-10}	9.58	
30.10	1.30×10^{-10}	9.89	
31.00	1.31×10^{-11}	10.88	
35.00	2.70×10^{-12}	11.56	
40.00	1.40×10^{-12}	11.85	

Typical points are calculated as follows:

1. Before the addition of any base the solution contains only HAc. The concentration of the acid is

$$\frac{(30)(0.1)}{100} = 3.00 \times 10^{-2} \text{ moles per liter}$$

If we let $X = [H^+]$ then $X = [Ac^-]$ and

$$\frac{X^2}{(3.00 \times 10^{-2}) - X} = 1.8 \times 10^{-5}$$

Throwing out[7] $-X$ from the denominator as insignificant

$$X^2 = 54 \times 10^{-8}$$
$$X = 7.35 \times 10^{-4}$$
$$pH = -\log 7.35 \times 10^{-4}$$
$$pH = 3.13$$

2. As an example of the calculation of a typical point after the titration has begun but before the stoichiometric point has been reached, suppose that 20 ml. of base has been added. Here we have free weak acid present plus salt of that acid; thus we have a buffer solution. Accordingly equation (25) applies for the calculation. We may think of the solution as consisting of 10 ml. of 0.1 *N* (= 0.1 *M*) free acid and 20 ml. of 0.1 *N* salt, diluted to a volume of 120 ml. Therefore,

$$[H^+] = \frac{\frac{10(0.1)}{120}}{\frac{20(0.1)}{120}} \cdot (1.8 \times 10^{-5})$$
$$= 1\tfrac{0}{20}(1.8 \times 10^{-5})$$
$$[H^+] = 9.00 \times 10^{-6}$$
$$pH = -\log 9.00 \times 10^{-6} = 5.05$$

[7] If $-X$ is not discarded we have a quadratic equation:

$$X^2 + 1.8 \times 10^{-5}X - (5.4 \times 10^{-7}) = 0$$

solved by applying the formula

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solving for X by the quadratic formula we find the value to be identical to two significant figures with the value obtained by the approximation. As a rule in such calculations the approximation is not valid if solving after discarding X to the first power yields a value for X which is appreciable in comparison with the term to or from which, in the original equation, it is added or subtracted. To illustrate, in

$$\frac{X^2}{0.2 - X} = 0.2$$

if the $-X$ is thrown out we have as an "approximation"

$$X^2 = (0.2)(0.2)$$
$$X = 0.2$$

whereas actually $X = 0.124$ (by quadratic solution). Therefore in this case, since the term from which X was subtracted in the original equation, namely 0.2, is appreciable in comparison with the value obtained by the approximation, also 0.2, we must solve by the exact method.

and similarly, after the addition of 25 ml. of base,

$$[H^+] = \tfrac{5}{25}(1.8 \times 10^{-5})$$
$$= 3.60 \times 10^{-6}$$
$$pH = -\log 3.60 \times 10^{-6} = 5.44$$

Equation (25), namely, $[H^+] \cong \frac{[HA]}{C} K_a$, it will be remembered, is only an approximation; it ignores the fact that [HA] is somewhat decreased and C is somewhat increased due to the slight ionization of the weak acid. Thus the true value of the numerator in equation (25) should be decreased to an extent governed by the degree of dissociation, and the denominator should be increased to an identical extent. The exact expression thus becomes, if we let X equal the dissociation of the acid in moles per liter, and thus also equal $[H^+]$,

$$X = \frac{[HA] - X}{C + X} \cdot K_a$$

or

$$X = -\left(\frac{C + K_a}{2}\right) + \sqrt{\frac{(C + K_a)^2}{4} + [HA]K_a} \tag{25a}$$

It is instructive to see just when equation (25) suffices and when equation (25a) is necessary. We may do this by calculating several points for Fig. 21 by both equations. If we do so the following values are obtained.

Table 11

VALUES OF pH CALCULATED APPROXIMATELY AND EXACTLY; HAc-NaOH TITRATION

Base Added, in ml.	*Approx.* pH *by Equation* (25)	*Exact* pH *by Equation* (25a)	*Difference* ΔpH
1. . .	3.28	3.43	0 15
2.	3.60	3.65	0.05
3. . . .	3.79	3.82	0 03
5. .	4.05	4.06	0.01
8	4.30	4 30	0.00
15	4.74	4 74	0 00

To illustrate the calculations by which the figures of the third column of Table 11 are obtained one such calculation is given. After 1.000 ml. of base has been added we have 29.00 ml. of acid remaining and also have 1.000 ml. of salt. The total volume of the solution is 101.0 ml. Therefore

$$[HA] = \frac{29.00(0.1000)}{101.0} = 2.87 \times 10^{-2}$$

and

$$C = \frac{1.000(0.1000)}{101.0} = 9.90 \times 10^{-4}$$

Substituting in equation (25a)

$$X = -\left[\frac{(9.90 \times 10^{-4}) + (1.8 \times 10^{-5})}{2}\right] + \sqrt{\frac{[(9.90 \times 10^{-4}) + (1.8 \times 10^{-5})]^2}{4} + (2.87 \times 10^{-2})(1.8 \times 10^{-5})}$$

$$= -5.04 \times 10^{-4} + 8.78 \times 10^{-4}$$

$$X = [H^+] = 3.74 \times 10^{-4}$$

$$pH = 3.43$$

It is seen from Table 11 that after 5 ml. of base has been added the exact equation (25a) is no longer needed. This, of course, is due to the fact that we are dealing with buffer solutions with a common ion effect and in the early stages of the titration the solution contains very little salt; therefore here the value of C in equation (25) *is* increased to a relatively great degree by the anion coming from the weakly dissociated acid. Likewise, when there is still little salt formed, the repression of the ionization of the acid is negligible, so that [HA] in equation (25) here must be significantly decreased, by the extent of its dissociation. Both of these corrections are made in equation (25a). But as larger quantities of base are added the amount of salt present increases, with the result that C more nearly approaches the value of the anion supplied by the salt alone, and the value of [HA] becomes (due to the common ion effect) more nearly that of the free acid alone. The net result of the exact calculation for the first few points in Fig. 21 is a steeper initial rise of the curve which, around 5 ml. of base in the example cited, gives way to a smaller slope (flatter curve) as the effectiveness of the buffer action becomes more pronounced.

It should be pointed out here that this same situation prevails for the initial stages of the titration when the weak acid is titrated with a weak base instead of with a strong base. If acetic acid is titrated with ammonium hydroxide we have present as the titration proceeds free acid and the salt, ammonium acetate, whereas with sodium hydroxide as the base we have present free acid and the salt, sodium acetate. In both instances then the components present in this region of the curves are a weak acid and a salt of the acid.

3. At the stoichiometric point equation (12) is used. The value of C is evidently $^{30}/_{130}(0.1) = 0.023$, so that

$$[H^+] = \sqrt{\frac{(10^{-14})(1.8 \times 10^{-5})}{2.3 \times 10^{-2}}}$$

$$[H^+] = 2.80 \times 10^{-9}$$

$$pH = -\log 2.80 \times 10^{-9} = 8.55$$

4. When excess base has been added the solution contains NaOH and NaAc. The hydrolysis of the salt thus is repressed and the pH is calculated exactly as for the corresponding point for the titration of a strong acid by a strong base. That is to say, the titration curve for a weak acid–strong base titration coincides with the curve for a strong acid–strong base titration after the stoichiometric point has been passed (base in the buret). This obviously must be true since in both cases the solution contains free base plus a salt: NaOH and NaAc in the one case, and NaOH and NaCl in the other.

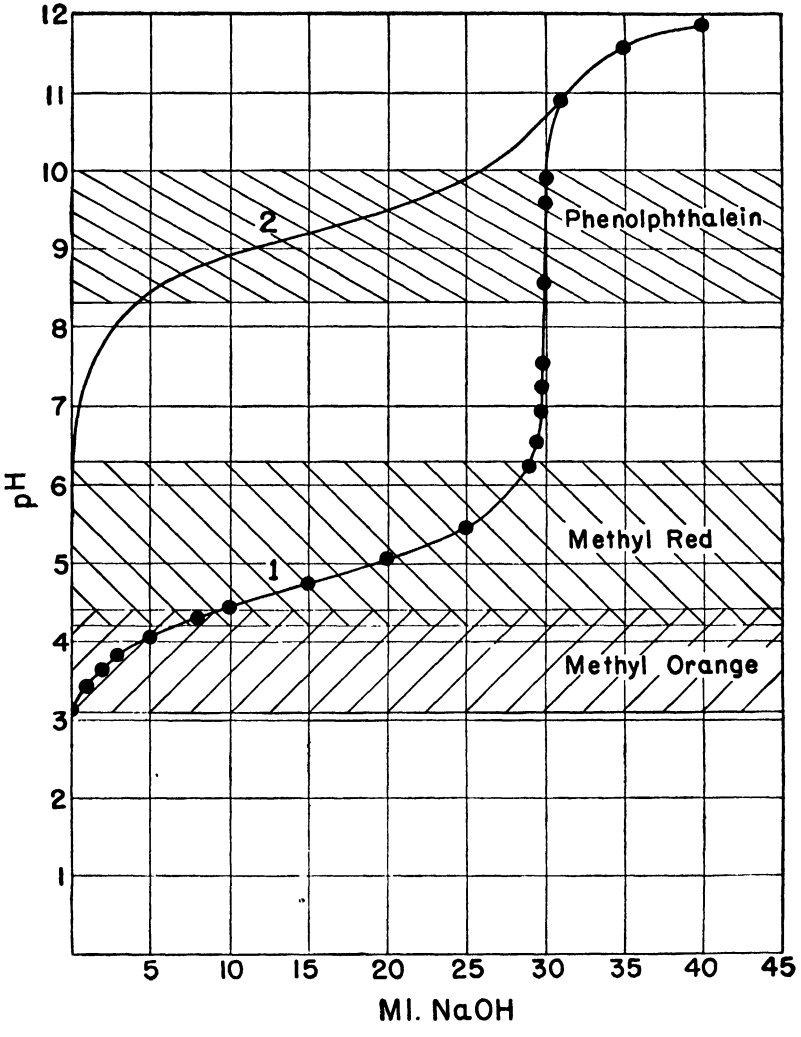


FIG. 21. Titration curves for $HC_2H_3O_2$ and H_3BO_3 with 0.1 *N* NaOH. Curve 1, 0.1 *N* $HC_2H_3O_2$ diluted from 30 ml. to 100 ml. before titrating; Curve 2, H_3BO_3. Note the rather pronounced change in slope of Curve 1 at about 5 ml. of NaOH (contrast this with the HCl-NaOH curve of Fig. 20 at 5 ml. of NaOH) due to the repression of the ionization of the weak acid by the salt, $NaC_2H_3O_2$, which by now has been formed in considerable quantity. From this point on to about 25 ml. of NaOH, both weak acid and salt of that acid are present in fair amounts; as a result the solution is buffered in this region. From 25 ml. to 30 ml. of base the buffer action again is very slight since only small amounts of acid remain, and the pH resumes its rapid rise with small increments of base.

The titration curve for acetic acid, Fig. 21, shows that, of the three indicators, phenolphthalein, methyl red and methyl orange, only the first may be used to detect the end point for the titration. Consider what would happen if one attempted the use of methyl orange. Since before any base has been added the solution of acetic acid already has a pH of 3.13, the color of the indicator, while predominantly pink, will be tinged with yellow. As base is added from the buret the color will gradually become more nearly pure yellow but the slow change in color will be extended over the addition of sodium hydroxide to about 10 ml. Thus there is no abrupt color change and even when the pure yellow does appear at a pH of about 4.4 only 30 per cent of the base necessary for chemical equivalence has been added. The titration error would amount to 70 per cent or 700 parts per 1000. Methyl red will not do either for it begins to change color at a pH of about 4.2 and becomes pure yellow when only 95 per cent of the theoretically equivalent quantity of base has been added. Thus a titration error of about 50 parts per 1000 results when it is used. Therefore, for such a weak acid as acetic acid an indicator like phenolphthalein with a narrow pH range occurring between 7 and 10.5 (the steep portion of the curve) must be employed. To summarize, methyl orange and methyl red fail as indicators for a weak acid–strong base titration because (a) the color change is not abrupt, and (b) even when the pure color is obtained only a fraction of the quantity of base necessary for chemical equivalence has been added. With phenolphthalein, however, the end point is sharp and is practically coincident with the stoichiometric point. Thymolphthalein also is satisfactory.

Titration of a Weak Base by a Strong Acid. The calculation of the points for the titration curve of a weak base–strong acid titration again involves the four types of points. Suppose 30 ml. of 0.1 *N* NH_4OH diluted to 100 ml. is titrated with 0.1 *N* HCl.

1. Before the addition of any acid from the buret the solution contains excess hydroxyl ion. The concentration of the base is

$$\frac{30(0.1)}{100} = 3.00 \times 10^{-2}$$

If $X = [OH^-]$ then $X = [NH_4^+]$ and

$$\frac{X^2}{(3.00 \times 10^{-2}) - X} = 1.8 \times 10^{-5}$$

$$X = 7.35 \times 10^{-4}$$

since

$$[H^+] = K_w/[OH^-]$$

$$[H^+] = \frac{10^{-14}}{7.35 \times 10^{-4}} = 1.36 \times 10^{-11}$$

$$pH = -\log 1.36 \times 10^{-11}$$

$$pH = 10.87$$

2. After the addition of HCl but before the stoichiometric point has been reached, for example, when 15 ml. of HCl has been added, from equation (26) we have

$$[H^+] = \frac{(15)(10^{-14})}{(15)(1.8 \times 10^{-5})}$$
$$= 5.56 \times 10^{-10}$$
$$pH = -\log 5.56 \times 10^{-10}$$
$$pH = 9.26$$

All that was said in regard to replacing buffer equation (25) with equation (25a) in calculating the exact pH for points up to 5 ml. of base in the titration of acetic acid with a strong base, must be borne in mind in constructing the present titration curve. Thus for the first several points for the ammonium hydroxide curve (up to 5 ml. of HCl) instead of equation (26), namely, $[H^+] \cong \frac{K_w C}{[BOH]K_b}$, one should use the more exact equation

$$X = -\left(\frac{C + K_b}{2}\right) + \sqrt{\frac{(C + K_b)^2}{4} + [BOH]K_b} \tag{26a}$$

and

$$[H^+] = \frac{K_w}{X},$$

where X represents $[OH^-]$. We arrive at equation (26a) by reasoning exactly analogous to that which leads to (25a). For comparison, after the addition of 1 ml. of HCl in our titration of ammonium hydroxide, equation (26) yields an approximate pH value of 10.72, whereas by the exact calculation the pH equals 10.57, a difference of 0.15 pH unit.

3. At the stoichiometric point equation (14) is used. The value of C is obviously $^{30}/_{130}(0.1)$ or 2.30×10^{-2} so that

$$[H^+] = \sqrt{\frac{(10^{-14})(2.30 \times 10^{-2})}{1.8 \times 10^{-5}}}$$
$$= 3.58 \times 10^{-6}$$
$$pH = -\log 3.58 \times 10^{-6}$$
$$pH = 5.45$$

4. When excess acid has been added, say 31 ml., the calculation of the pH is analogous to corresponding points of previous titration curves. The solution contains salt and free acid, considered to be completely ionized. Therefore

$$[H^+] = \frac{1(0.1)}{131} = 7.63 \times 10^{-4}$$
$$pH = -\log 7.63 \times 10^{-4}$$
$$pH = 3.12$$

Table 12 lists the calculated pH for 18 points for this titration. These are plotted in Fig. 22. By arguments similar to those given for other titra-

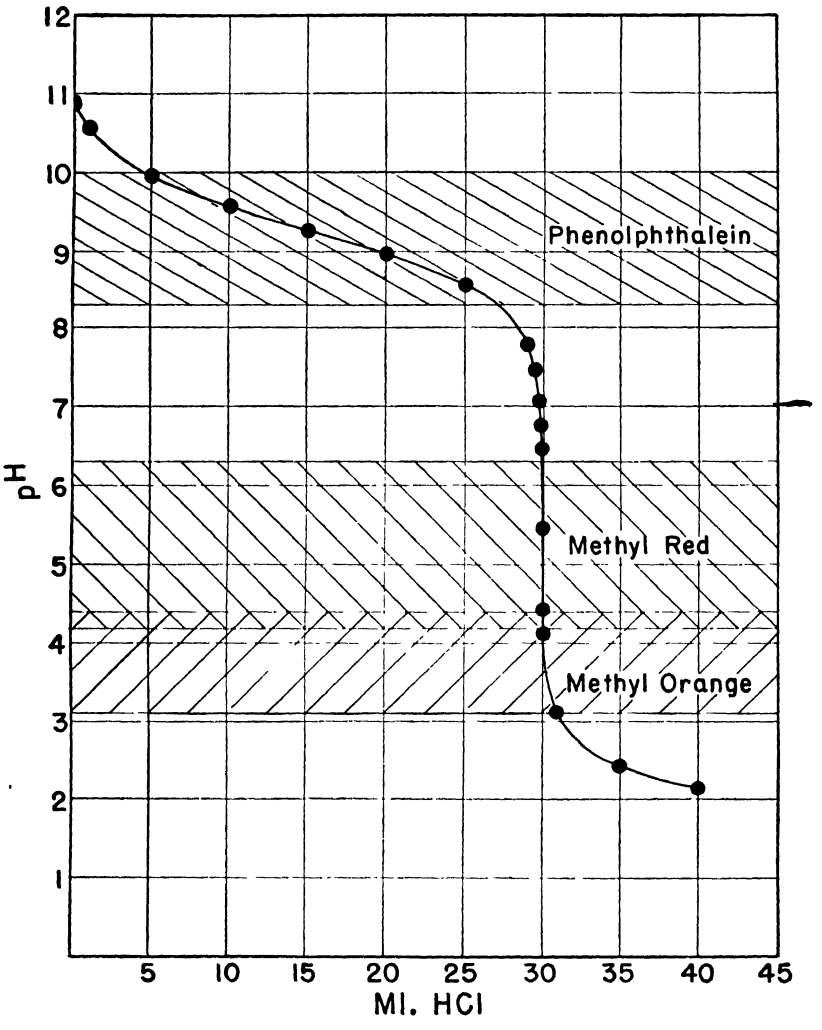


FIG. 22. Titration curve for NH_4OH with 0.1 *N* HCl. Thirty ml. of 0.1 *N* NH_4OH diluted to 100 ml. before titrating.

Note the rather pronounced change of slope at about 5 ml. of HCl due to the repression of the ionization of the weak base by the salt, NH_4Cl, which by now has been formed in considerable quantity. From this point on to about 25 ml. of HCl both weak base and salt of that base are present in fair amounts; as a result the solution is buffered in this region. From 25 ml. to 30 ml. of acid the buffer action again is very slight since only small amounts of base remain and the pH resumes its rapid fall with small increments of acid.

tions and by inspection of this curve it should be clear that phenolphthalein cannot be used as the indicator in the titration of such a weak base as ammonium hydroxide by hydrochloric acid, and that either methyl red or methyl orange may be used, preferably the former.

Table 12

TITRATION OF 0.1 *N* NH_4OH BY 0.1 *N* HCL. 30 ML. OF 0.1 *N* NH_4OH DILUTED TO 100 ML. CALCULATED VALUES OF pH

Acid Added in ml.	$[H^+]$ by *Equa.* (26)	pH by *Equa.* (26)	pH by *Equa.* (26a)
0.00	1.36×10^{-11}	10.87	
1.00	1.92×10^{-11}	(10.72)	10.57
5 00	1.11×10^{-10}	9.95	
10 00	$2\ 77 \times 10^{-10}$	9.56	
15.00	5.56×10^{-10}	9 26	
20.00	1.11×10^{-9}	8.95	
25 00	2.78×10^{-9}	8 56	
29 00	1.61×10^{-8}	7.79	
29 50	3.28×10^{-8}	7.48	
29 80	8.26×10^{-8}	7.08	
29 90	1.66×10^{-7}	6.77	
29 95	3.33×10^{-7}	6.48	
30 00	3.58×10^{-6}	5.45	
30 05	3.85×10^{-5}	4.42	
30.10	7.69×10^{-5}	4.11	
31.00	7.63×10^{-4}	3.12	
35.00	3.70×10^{-3}	2.43	
40.00	7.14×10^{-3}	2.15	

Titration of a Weak Base by a Weak Acid. Salts of weak acids and weak bases hydrolyze to a considerable extent; therefore, in the titration of a weak base and a weak acid hydrolysis plays an unusually important role. The pH at the stoichiometric point depends upon the relative values of K_b and K_a. If K_b and K_a are equal the titration results in a pH of 7.0 at the stoichiometric point. There will be practically no steep portion to the titration curve (see Fig. 23), and thus no color indicator will reveal the end point distinctly. Such titrations may be made potentiometrically but reliable results cannot be obtained colorimetrically. Nevertheless much can be learned by constructing the titration curve. Suppose, as usual, we consider 30 ml. of 0.1 *N* $HC_2H_3O_2$ diluted to 100 ml. and titrated with 0.1 *N* NH_4OH.

1. The calculation of the pH in the beginning, before any base has been added, is, of course, identical with that already made for the acetic acid–sodium hydroxide titration. The pH is 3.13.

2. The solution corresponding to all other points preceding the stoichiometric point consists of free acetic acid and the salt, ammonium acetate—that is, a weak acid and a salt of that acid. The solution therefore is a buffer. Accordingly, the calculations of these points of the titration curve are made in the same manner as those for the titration of acetic acid with sodium hydroxide as computed by equations (25) and (25a). The two curves are identical for corresponding additions of base up to a volume of 29.0 ml.

At about 29.0 ml. of base, however, a difference in the two curves begins to reveal itself. Anticipating the stoichiometric point for the present titration, it is foreseen that the pH will be 7.0 since acetic acid and ammonium hydroxide have ionization constants almost identical, 1.8×10^{-5}. It follows then that the acetic acid–ammonium hydroxide titration cannot possibly yield a solution with a pH as great as 7.0 before 30 ml. of base has been added. In the case of the acetic acid–sodium hydroxide titration after 29.90 ml. of base the pH was calculated as 7.22. Obviously then equation (25) will not serve for computing the pH for a weak acid–weak base titration for points on the acid side but *very close to the stoichiometric point.* Two questions arise then: why does equation (25) fail here, and how *may* the calculation be made?

Recalling equation (25) it will be remembered that no account of hydrolysis was taken. But the salt of a weak acid and a weak base hydrolyzes to such an extent, even in the presence of a small quantity of acid or base, that this simplified equation is no longer strictly valid. If a solution of such a salt contains also an excess of weak acid, of concentration a, the total concentration of HA will be $a + y$, where y is the concentration of HA formed by hydrolysis of the salt; and equation (25) must be replaced by the more exact expression

$$[H^+] = \frac{a + y}{C - y} \cdot K_a$$

or, since near the stoichiometric point C is *very* great compared with y,

(25b)
$$[H^+] = \frac{a + y}{C} \cdot K_a$$

It is necessary to find the value of y before equation (25b) may be used. This may be done by rearranging equation (17), namely,

$$\frac{[BOH][HA]}{[B^+][A^-]} = \frac{K_w}{K_a K_b},$$

taking into consideration that the acid concentration is greater than [HA] by y, the concentration of HA due to hydrolysis. Then also [BOH] will be equal to y and since $[B^+] = [A^-] = C - y$ we have

(17a)
$$\frac{y(a + y)}{(C - y)^2} = \frac{K_w}{K_a K_b}$$

or, since near the stoichiometric point C is great compared with y, we have the excellent approximation[8]

[8] y may be discarded in the denominator but not in the numerator because near the stoichiometric point the concentration of the acid, a, is small, whereas that of the salt, C, is large. Thus $(C - y)$ is practically identical with C, but $(a + y)$ is by no means equal to a.

$$\frac{y(a+y)}{C^2} \cong \frac{K_w}{K_a K_b}$$

In solving for y the above equation may be put into the form

$$y^2 + ay - \frac{C^2 K_w}{K_a K_b} = 0$$

from whence

$$y = -\frac{a}{2} + \sqrt{\frac{a^2}{4} + \frac{C^2 K_w}{K_a K_b}} \tag{31a}$$

Once y is determined it may be inserted into equation (25b) and the value of $[H^+]$ and then of pH may be obtained.

Suppose we calculate y in the titration of our acetic acid solution after the addition of 29.90 ml. of ammonium hydroxide, that is, when 0.10 ml. of acid remains.

$$a = \frac{(0.1000)(0.1000)}{129.9} = 7.70 \times 10^{-5}$$

$$C = \frac{(29.90)(0.1000)}{129.9} = 2.30 \times 10^{-2}$$

Substituting in equation (31a),

$$y = -\frac{7.70 \times 10^{-5}}{2} + \sqrt{\frac{(7.70 \times 10^{-5})^2}{4} + \frac{(2.30 \times 10^{-2})^2 (10^{-14})}{(1.8 \times 10^{-5})(1.8 \times 10^{-5})}}$$

$$= -3.85 \times 10^{-5} + 13.35 \times 10^{-5}$$

$$y = 9.50 \times 10^{-5}$$

And substituting this value of y in equation (25b),

$$[H^+] = \left[\frac{(7.70 \times 10^{-5}) + (9.50 \times 10^{-5})}{2.30 \times 10^{-2}}\right]\left[1.8 \times 10^{-5}\right]$$

$$[H^+] = 1.35 \times 10^{-7}$$

$$pH = 6.87$$

This compares with a pH value of 7.22 (see Table 10) which would be obtained by using equation (25). In constructing the curve of Fig. 23 the value, 6.87, has been used for the addition of 29.90 ml. of base. Equations (31a) and (25b) must be employed if the degree of hydrolysis is 5 per cent or greater. The simpler equation (25) suffices for points more removed from the stoichiometric point than 0.1 ml. in such a titration as we have considered because hydrolysis is repressed when considerable quantity of acid (or base) is present. To demonstrate this fact the pH may be calculated by equations (31a) and (25b), and again by equation (25), for the addition of 20 ml. of ammonium hydroxide. By either method a pH of 5.05 is obtained. Even with only 1 ml. of acetic acid remaining (after the addition of 29 ml. of base), the pH calculated by either method is found to be 6.21.

3. At the stoichiometric point equation (18) gives the value of $[H^+]$

$$[H^+] = \sqrt{\frac{(10^{-14})(1.8 \times 10^{-5})}{1.8 \times 10^{-5}}}$$

$$[H^+] = 10^{-7}$$

$$pH = 7.00$$

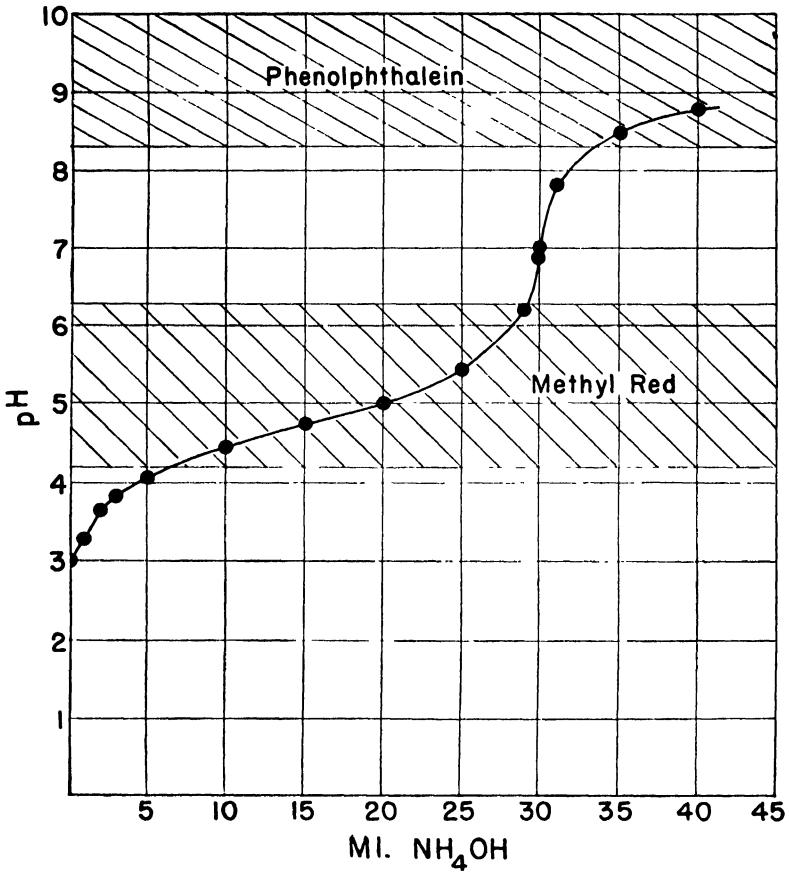


FIG. 23. Titration curve for $HC_2H_3O_2$ with 0.1 *N* NH_4OH. Thirty ml. of 0.1 *N* $HC_2H_3O_2$ diluted to 100 ml. before titrating.

4. When excess ammonium hydroxide has been added the solution contains free weak base and its salt; therefore buffer equation (26) may be used except when very near the stoichiometric point where a more exact form must be used, that is

$$[H^+] = \frac{K_a C}{(b + y)K_b} \tag{26b}$$

where b is the concentration of the excess base and y is the concentration of BOH due to hydrolysis. The derivation is analogous to that of equation (25b). The value of y is obtained in the same manner as y of equation (31a) and its formulation evidently becomes

$$y = -\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{C^2 K_w}{K_a K_b}} \tag{31b}$$

To illustrate, when 30.10 ml. of ammonium hydroxide is added to the acetic acid solution, equation (26b) leads to a pH value of 7.13 which is 0.13 unit on the basic side of neutrality, the same extent by which 29.90 ml. of ammonium hydroxide

failed to reach neutrality in this titration. The detailed calculation follows. We have present in the solution 0.10 ml. of excess base and 30 ml. of salt in a total volume of 130.1 ml.

$$b = \frac{(0.1000)(0.1000)}{130.1} = 7.69 \times 10^{-5}$$

$$C = \frac{(30.00)(0.1000)}{130.1} = 2.31 \times 10^{-2}$$

Therefore,

$$y = -\frac{7.69 \times 10^{-5}}{2} + \sqrt{\frac{(7.69 \times 10^{-5})^2}{4} + \frac{(2.31 \times 10^{-2})^2 (10^{-14})}{(1.8 \times 10^{-5})(1.8 \times 10^{-5})}}$$

$$= -3.84 \times 10^{-5} + 13.39 \times 10^{-5}$$

$$y = 9.55 \times 10^{-5}$$

and substituting this value of y in equation (26b)

$$[H^+] = \frac{(10^{-14})(2.31 \times 10^{-2})}{[(7.69 \times 10^{-5}) + (9.55 \times 10^{-5})][1.8 \times 10^{-5}]}$$

$$[H^+] = 7.44 \times 10^{-8}$$

$$pH = 7.13$$

The simplified equation (26) leads to the same pH values as does the more exact calculation when the stoichiometric point has been passed to an extent of 1 ml. or more of ammonium hydroxide. This means of course that the hydrolysis is repressed enough in the presence of greater amounts of base so that equation (26) is sufficiently accurate.

The curve of Fig. 23 shows that there is no abrupt change in pH around the stoichiometric point. Thus it is impossible to find an indicator which will detect the end point for a weak acid–weak base titration, and such titrations are not attempted. It should be noted that the first part of a titration curve of this type resembles that of a weak acid–strong base from the beginning of the curve until near the stoichiometric point. Furthermore this curve resembles that of a strong acid–weak base titration (if base is in the buret) in that part shortly after the stoichiometric point has been passed and on to points corresponding to considerable excess base. The question might arise then as to why we could not employ successfully an indicator with a pH range from about 6.5 to 7.5 to mark the end point of a weak acid–weak base titration. The answer is that in the vicinity of the stoichiometric point this curve is not rising so abruptly (as the exact calculations of pH for 29.90 and 30.10 ml. of base have shown) as that resulting when either the acid or the base is strong. Thus an indicator, even though giving a color change between pH 6.5 and 7.5, would not be satisfactory since it would not give a sharp end point.

Other Titrations. Very Weak Acids, Polybasic Acids and Carbonates. The weaker the acid being titrated the higher will be the initial pH. Thus the titration curves show less abrupt change of slope at the stoichiometric point, and in order for such titrations to be feasible more and more sensitive indicators are needed. Boric acid which has a value of

K_a of 6×10^{-10} cannot be titrated. See Fig. 21. However, if glycerol or mannitol is added the boric acid is converted into complex acids which are much stronger than boric acid itself. Under such conditions a good break in the curve is obtained and phenolphthalein can be used as an indicator.

When polybasic acids are titrated with a strong base breaks may occur corresponding to each step in the ionization of the acid. However, the breaks in the curve appear as distinct steps only if the two or more ionization constants differ widely in magnitude ($K_{a_1}/K_{a_2} \gtrsim 10^4$). Thus sulfuric acid, though dibasic, acts like a monobasic acid since both steps in its ionization are fairly complete. On the other hand, phosphoric acid gives two rather distinct breaks in its titration curve, but not three. The first break, Fig. 24, comes after the first hydrogen has reacted, the second break when the second hydrogen has reacted, but there is no break indicating the reaction of the third hydrogen. These facts are understood when it is realized that K_{a_1} and K_{a_2} for phosphoric acid have values around 10^{-3} and 10^{-8} respectively, and the third ionization constant, $K_{a_3} = 10^{-13}$, is near the value of K_w. A solution of Na_3PO_4 is strongly hydrolyzed, which is another way of saying that the trisodium salt will not be formed by the reaction of the HPO_4^- ion with sodium hydroxide. The curve in Fig. 24 for phosphoric acid exhibits the first break at a pH near 4 and the second at around 9. Thus methyl orange and phenolphthalein serve to indicate these two stoichiometric points; the volume of base necessary for the methyl orange end point is approximately one-third the quantity, and that necessary for the phenolphthalein end point is approximately two-thirds the quantity, of base equivalent to all of the replaceable hydrogen.

A carbonate may be titrated by strong acids and two successive reactions occur:

$$CO_3^- + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

The second of the above reactions does not occur as long as any CO_3^- ion remains in the solution. When enough acid has been added to satisfy the first reaction we find a break in the titration curve results. The further addition of acid causes the formation of carbonic acid and at the completion of the second reaction a second break in the titration curve is found. The pH values at the two breaks are calculable. That established by the bicarbonate ion has already been computed (p. 97) and found to be 8.4. (If the titration is sodium carbonate against hydrochloric acid the solution will contain, when the first stoichiometric point is reached, sodium bicarbonate and sodium chloride, but the latter will have no effect upon the pH.) Therefore phenolphthalein may be used to detect this end point. The pH of the solution corresponding to the second break in the curve is

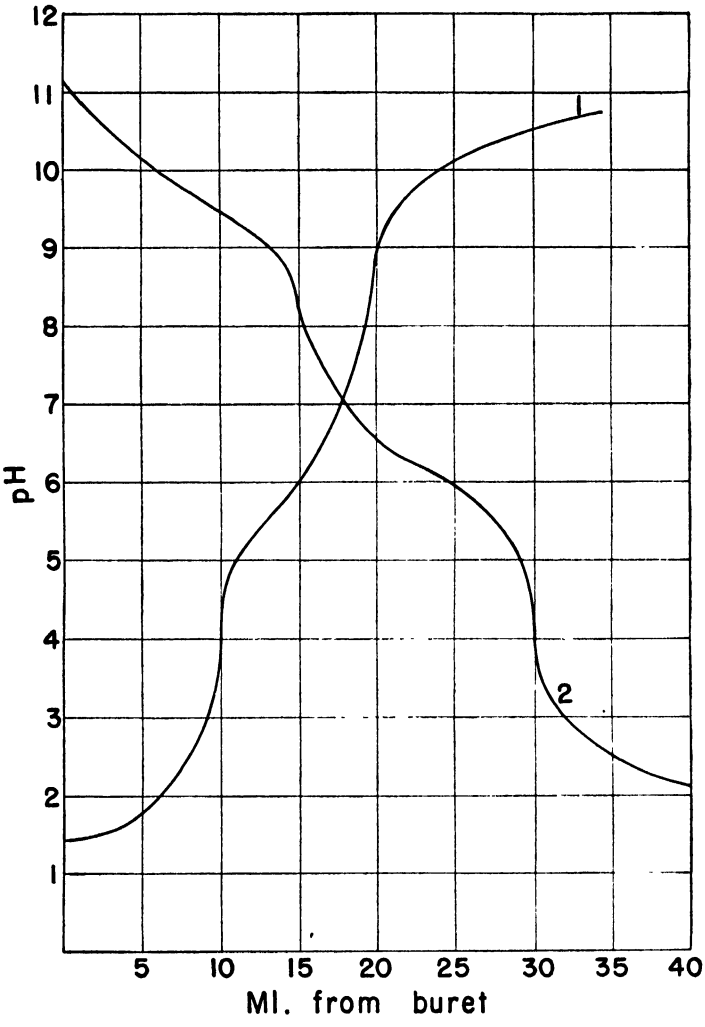


FIG. 24. Titration curves for H_3PO_4 with 0.1 *N* NaOH (Curve 1) and for Na_2CO_3 with 0.1 *N* HCl (Curve 2).

calculated by means of equation (6a). If the titration were 30 ml. of 0.1 *N* Na_2CO_3 diluted to 100 ml. against 0.1 *N* HCl the concentration of carbonic acid would be

$$\frac{30(0.1)}{(130)2} = 1.16 \times 10^{-2}\ M$$

Therefore

$$[H^+] = \sqrt{CK_{a_1}} = \sqrt{(1.16 \times 10^{-2})(3.0 \times 10^{-7})}$$
$$[H^+] = 5.9 \times 10^{-5}$$
$$pH = 4.2$$

This value comes within the range of methyl orange so that it may be used as the indicator for the second step. Obviously carbonates may be titrated first using phenolphthalein and then, after the red color has disappeared upon the addition of acid, using methyl orange. The volume of acid needed to reach the methyl orange end point will be just about double the volume necessary to reach the phenolphthalein end point. Fig. 24 shows the curve for sodium carbonate titrated with hydrochloric acid.

The two end points in a carbonate titration make possible so-called double titrations, in which carbonate and hydroxide, or carbonate and bicarbonate, or hydroxide and bicarbonate,[9] may be determined in the presence of one another. Suppose a mixture of sodium carbonate and sodium hydroxide is brought into solution and titrated with standard hydrochloric acid. The following reactions will occur

$$(1)\ NaOH + HCl \rightarrow NaCl + H_2O$$
$$(2)\ Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
$$(3)\ NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$$

At the start of the titration the pH of the solution will be around 11 or above and phenolphthalein will impart its red color to the solution. When enough acid, say A ml., has been added to complete reaction (1) and (2), the pH of the solution will be that due to sodium bicarbonate, or about 8.4, and the red color practically disappears. If now methyl orange is added the color will be orange; further addition of acid until the red color of methyl orange appears, say B ml., marks the completion of reaction (3). The A ml. of acid obviously is the volume necessary to react with all the sodium hydroxide plus half enough for complete reaction with the carbonate. The additional B ml. of acid is the volume necessary to convert the bicarbonate to carbonic acid, or 2B ml. is equivalent to all of the sodium carbonate. Thus (A + B) − 2B, or A − B ml. of acid are equivalent to the sodium hydroxide. From these volumes, A − B ml. and 2B ml., and the normality of the acid, the amount of sodium hydroxide and sodium carbonate in the sample may be calculated.

[9] Mixtures of NaOH and $NaHCO_3$ are not encountered in solution because hydroxyl and bicarbonate ions react: $OH^- + HCO_3^- \rightarrow CO_3^- + H_2O$. However, a dry mixture of the two can be analyzed by the double-titration method since, even though when brought into aqueous solution the above reaction takes place, the stoichiometric relationship between the titrating acid and the ions actually present in the solution will be the same as if the above reaction had not taken place. For example, suppose a dry mixture contains one mole each of hydroxide and of bicarbonate. Obviously one mole of a monobasic acid is equivalent to each of the two components or two moles to the whole mixture. In solution, however, the hydroxide and bicarbonate react to form a mole of sodium carbonate. To titrate one mole of carbonate a mole of acid is necessary to satisfy the titration to the phenolphthalein end point, and an additional mole is necessary to carry the titration (of the bicarbonate now formed from the carbonate) to the methyl orange end point. Thus the stoichiometric relationship is the same as it would have been had no reaction taken place initially between OH^- and HCO_3^-.

The phenolphthalein end point in the above double titration is not very sharp and a precision of better than 5 or 10 parts per 1000 can hardly be obtained. Better results may be had if two aliquot portions of the solution of mixed alkalies are used. The total of carbonate and hydroxide is first determined by titration against standard acid to the methyl orange end point. Then, using the other portion, the carbonate is precipitated by adding a slight excess of barium chloride, and the hydroxide alone is determined by titrating with acid to the phenolphthalein end point. The precipitated barium carbonate need not be filtered off since at the phenolphthalein end point the pH is sufficiently high to prevent the barium carbonate from dissolving.

Problem. A sample of a mixture of NaOH, Na_2CO_3 and inert material weighing 0.2375 g. requires 34.06 ml. of 0.0960 *N* HCl to reach the phenolphthalein end point and an additional 13.78 ml. to reach the methyl orange end point. What is the per cent NaOH and Na_2CO_3 in the sample?

Solution (*a*). Here A ml. = 34.06 and B ml. = 13.78.

Therefore $2B = 27.56$ ml. acid equivalent to Na_2CO_3.

$A - B = 20.28$ ml. acid equivalent to NaOH.

$N \cdot V = N' \cdot V'$

$(0.0960)(27.56) = N' 1000$

$N' = 0.002646$ = normality with respect to Na_2CO_3, assuming the sample is dissolved in 1 l. of solution.

$N \cdot V = N' \cdot V'$

$(0.0960)(20.28) = N' 1000$

$N' = 0.001947$ = normality with respect to NaOH, assuming the sample is dissolved in 1 l. of solution.

$$\frac{(0.002646)(53.00)(100)}{0.2375} = 59.0\%\ Na_2CO_3$$

$$\frac{(0.001947)(40.01)(100)}{0.2375} = 32.8\%\ NaOH$$

Solution (*b*). The problem may be solved directly in terms of gram equivalent weights in the following manner.

The g. eq. wts. of Na_2CO_3 present in the mixture must be equal to (0.02756)(0.0960) since this is the g. eq. wt. of acid necessary to react with the carbonate. The equivalent weight of Na_2CO_3 is 53.00. Therefore

$$\frac{(0.02756)(0.0960)(53.00)(100)}{0.2375} = 59.0\%\ Na_2CO_3$$

In a like manner

$$\frac{(0.02028)(0.0960)(40.01)(100)}{0.2375} = 32.8\%\ NaOH$$

Use of Carbon Dioxide–Free Water. Since the atmosphere always contains some carbon dioxide, solutions exposed to air will absorb the gas and form carbonic acid. In acid-base titrations the dissolved carbon dioxide will make no difference if, for example, methyl orange or methyl red is used as the indicator. If, however, an indicator like phenolphthalein is

used it is necessary to employ carbon dioxide–free water in the titration. Consider an acid being titrated with sodium hydroxide and suppose that the solution of the acid also contains carbon dioxide. When a quantity of base chemically equivalent to the acid has been added the next excess drop of sodium hydroxide should elevate the pH to a point where the phenolphthalein becomes red, thus marking the end of the titration. With carbonic acid present, however, the "excess" drop of sodium hydroxide will react with the carbonic acid to form sodium bicarbonate. Further addition of base results in the formation of more bicarbonate until finally no more carbonic acid remains. The pH at this point will be that established by bicarbonates—namely, about 8.4—so that the phenolphthalein is still colorless. The next drop of base will form sodium carbonate, Na_2CO_3, and even in small concentration the presence of the normal carbonate will bring the pH up to the phenolphthalein range and, at last, the red color appears. However, by this time an amount of base has been added in excess of the amount equivalent to the acid being titrated by just that quantity necessary to convert the carbonic acid into bicarbonate. A considerable error thus has been introduced. Had methyl orange been used as the indicator, the formation of the first of the bicarbonate would have caused the pH to be on the orange side of the indicator and no harm would have resulted. Since indicators with a high pH range must be used in the titration of weak acids by strong bases it follows that carbon dioxide–free water[10] must be employed in such cases. In general one should use carbon dioxide–free water if the indicator employed changes color at a pH above 8.4, i.e., that established by bicarbonates.

Summary on Titration Curves

It is worth repeating that for the calculation of the pH of the solution being titrated there are, in general, four typical calculations to be made. These are: (1) the pH of the solution before the addition of any reagent from the buret; (2) the pH after the addition of reagent from the buret but before the stoichiometric point has been reached; (3) the pH at the stoichiometric point; (4) the pH after excess reagent has been added. The method of making the above four kinds of calculations has been explained (a) for the titration of a strong acid with a strong base, (b) for the titration of a weak acid with a strong base, (c) for the titration of a weak base with a strong acid and (d) for the titration of a weak acid with a weak base.

In addition to the four typical calculations listed above, in which it is sufficient to employ equations which are sometimes close approximations

[10] Prepare carbon dioxide–free water as follows: Place about 4.5 l. of distilled water in a 5 l. pyrex flask and boil to expel CO_2. Insert a two-hole rubber stopper equipped with a siphon and a soda-lime tube.

only, there are a few instances in which approximate equations are not valid enough to reveal the exceptional nature of the calculation involved. The exceptions are as follows. (1) For the calculation of $[H^+]$ in the titration of a weak acid by any base, in the *early stages* of the titration, instead of equation (25) one must use (25a). (2) Likewise, for calculation of $[OH^-]$ (and thence $[H^+]$) of the solution in the titration of a weak base with any acid, in the *early stages* of the titration, instead of equation (26) one must use (26a). (3) In the titration of a weak acid by a weak base (not practicable, of course, with color indicators), in addition to exceptions (1) and (2) just cited, the calculation of $[H^+]$ established *just before* and *just after* the stoichiometric point must be made by using, instead of equations (25) and (26) respectively, equations (25b) and (26b).

The conditions under which the two buffer equations, (25) and (26), do not lead to good approximations of the hydrogen ion concentration, and the more exact equations which, under these conditions, replace them, are brought together below.

Equation (25) $[H^+] \cong \frac{[HA]}{C} \cdot K_a$. Acid buffer; no complications.

Equation (25a) $$X = [H^+] = -\left(\frac{C + K_a}{2}\right) + \sqrt{\frac{(C + K_a)^2}{4} + [HA]K_a}$$

Use instead of (25) for exact $[H^+]$ for points in *early stages* of weak acid–base titration.

Equation (25b) $$[H^+] = \frac{a + y}{C} \cdot K_a$$

Use instead of (25) for exact $[H^+]$ for points *near stoichiometric point* (on *acid* side) in weak acid–weak base titration. (Obtain y from (31a).)

Equation (26) $[H^+] \cong \frac{K_w C}{[BOH]K_b}$. Basic buffer; no complications.

Equation (26a) $$X = [OH^-] = -\left(\frac{C + K_b}{2}\right) + \sqrt{\frac{(C + K_b)^2}{4} + [BOH]K_b}$$

Use instead of (26) for exact $[OH^-]$ (whence exact $[H^+]$) for points in *early stages* of weak base–acid titration.

Equation (26b) $$[H^+] = \frac{K_w C}{(b + y)K_b}$$

Use instead of (26) for exact $[H^+]$ for points *near stoichiometric point* (on *basic* side) in weak acid–weak base titration. (Obtain y from (31b).)

Equation (31a) $$y = -\frac{a}{2} + \sqrt{\frac{a^2}{4} + \frac{C^2K_w}{K_aK_b}}$$

Use in connection with (25b).

Equation (31b) $$y = -\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{C^2K_w}{K_aK_b}}$$

Use in connection with (26b).

Questions and Problems

(See Appendix for ionization constants)

1. Calculate the pH established by the following solutions:
   (a) A 0.02 *N* solution of sodium benzoate.
   (b) A 0.1 *N* solution of ammonium fluoride.
   (c) A solution of potassium bitartrate of moderate concentration.
   (d) A solution which is 0.123 *N* with respect to benzoic acid and 0.246 *N* with respect to sodium benzoate.
   (e) One hundred ml. of a solution identical with that of (d) except that it also contains 10 ml. of 0.1 *N* hydrochloric acid.
   Answer to (d): 4.5.
2. The ionization constant of a weak acid, HA, is 1.86×10^{-5}. Calculate the pH of a 0.1 *N* solution.
   Answer: 2.87.
3. The ionization constant of a weak base, BOH, is 3×10^{-6}. Calculate the pH of a 0.1 *N* solution.
4. (a) Twenty-five ml. of a 0.1 *N* solution of a weak acid ($K = 10^{-6}$) is diluted to 100 ml. and titrated with 0.1 *N* potassium hydroxide solution. Calculate the approximate pH of the solution resulting from the titration at a sufficient number of points to reveal the path of the titration curve. Plot these points on graph paper. (b) Repeat (a) using 0.01 *N* solutions of both acid and base. (c) What indicator would you select for the titration of (a)? Would the same indicator be suitable for the titration of (b)?
5. Derive equation (25a) from equation (25) after inserting into the latter the more exact expressions which take into account the slight ionization of the weak acid. (Cf. p. 111.)
6. (a) In the titration of 4(a) above what is the difference in the value of the pH as calculated by equation 25 and by equation (25a) after the addition of 1.00 ml. of base? (b) How does this difference, Δ pH, vary for a given small addition of base to weak acids having different values for K_a?
   Answer to (a): Δ pH = 0.10.
7. When distilled water is exposed at room temperature to the atmosphere it will absorb carbon dioxide to the extent of about 0.000014 mole per liter. Calculate the pH of the water.
   Answer: 5.7.
8. Explain the type and extent of the error introduced in titrating a weak acid with sodium hydroxide solution when the solution also contains dissolved carbon dioxide.

9. A solution is made up by diluting exactly 5 ml. of 0.1 *N* hydrochloric acid to 100 ml. (a) Calculate the pH of the solution. (b) How many grams of solid sodium acetate, $NaC_2H_3O_2$, must be added to this solution (assume that the volume remains constant at 100 ml.) in order to change the pH to a value of 4.66?

   Answer: (a) 2.3; (b) 0.0745 g.

10. (a) A solution is prepared by diluting 2.5 ml. of 0.2 *N* sodium hydroxide to 100 ml. Calculate the pH of the solution. (b) How many grams of solid ammonium acetate must be added to this solution in order to change the pH to a value of 9.34?

11. A 0.025 *M* solution of the sodium salt of a certain weak acid has a pH of 8.57. Calculate the value of K_a for the acid.

    Answer: 1.8×10^{-5}.

12. A solution of the ammonium salt of a certain weak acid has a pH of 6.75. Calculate the value of K_a for the acid.

Chapter 8

ACIDIMETRY AND ALKALIMETRY

IN DETERMINING the acid or base present in a sample unknown in respect to one of these constituents it is only necessary to learn what quantity of a standard solution of a base or an acid is required to react with the unknown. Thus it is customary to have on hand a standard solution of an acid and a base which may be used in such determinations. The acid most commonly employed is hydrochloric although sometimes sulfuric and oxalic acids are used. The last two are not volatile and accordingly may be boiled, if desired, with the unknown without loss. The base most commonly used as a standard solution is sodium hydroxide but potassium hydroxide and barium hydroxide often are chosen. The standardization of the solution, acid or base, simply involves the titration of the solution against an accurately weighed quantity of some basic or acidic substance which meets the criteria already listed on p. 78 for primary standards. Of course, once a solution of either has been standardized, it may be titrated against the solution of the other and the normality of the latter thus determined. In this case, however, the concentration of the latter has been ascertained through a secondary standardization and the accuracy of the normality is subject to greater error than when a primary standardization has been carried out. In the following sections directions will be given for the standardization of a hydrochloric acid solution and for a sodium hydroxide solution, both about 0.1 N; also the procedures for certain analyses in which these two standard solutions are used. It should be obvious that standard solutions which are about 0.1 N will yield more accurate results in analyses than, say, 0.5 N solutions since a given weight of an unknown will require five times the volume in the former case. The amount of the sample taken for analysis and the concentration of the standard solution used should be such that, as a rule, a titrating volume of from 30 to 50 ml. will result. Too small a titrating volume may introduce an unnecessarily large error, and volumes over 50 ml. require refilling a 50 ml. buret which also increases the chance of error.

PREPARATION OF 0.1 N HYDROCHLORIC ACID SOLUTION

The object is to prepare a solution of hydrochloric acid which will be in the neighborhood of 0.1 N, and then to learn through its standardization exactly (with a precision of about 1 part per 1000 possible deviation)

what the normality is. The equivalent weight of hydrochloric acid is approximately 36.5, so that the solution which is prepared must contain around 3.65 g. of hydrogen chloride per liter of solution. From Table 6, p. 84, we learn that 1 ml. of concentrated hydrochloric acid contains 0.43 g. of HCl. Thus to make 1 l. of 0.1 *N* solution we shall need about 8.5 ml. of the concentrated acid.

Procedure. With a graduated cylinder, measure 9 ml. of concentrated hydrochloric acid and transfer to a 1 l. glass-stoppered bottle. Add about 1 l. of carbon dioxide–free water and shake thoroughly. Keep the bottle stoppered at all times. After filling a buret with the solution always replace the stopper in the bottle at once since evaporation would cause a change in the normality. If desired, the bottle may be equipped with a siphon for delivery; in that case use a two-hole rubber stopper and insert a soda-lime tube to prevent the entry of carbon dioxide and moisture from the air.

PREPARATION OF 0.1 *N* SODIUM HYDROXIDE SOLUTION

Standard solutions of sodium hydroxide cannot be prepared directly —i.e., by weighing the hydroxide accurately, dissolving and diluting to proper volume—because it is hygroscopic and because it always contains some sodium carbonate. In some analyses it is necessary to use carbonate-free sodium hydroxide solution; it therefore is well to prepare a solution containing little or no carbonate. This may be done by adding to an ordinary solution of sodium hydroxide which is contaminated with some carbonate, sufficient barium chloride to precipitate the carbonate. The solution is then filtered through asbestos in a Gooch crucible. This method of course calls for a slight excess of barium chloride; if this is objectionable the method given in the procedure below is recommended.

Procedure. Into a warmed clean bottle of 1000 to 1200 ml. capacity pour about 50 ml. of melted paraffin. Turn the bottle on its side and roll so that as the wax solidifies it coats the inside of the bottle. While some of the paraffin is still liquid turn the bottle upright so that the bottom receives a coating of wax.[1] When cool pour in a liter of freshly boiled and cooled, distilled water (carbon dioxide–free water).

Prepare a Gooch crucible with an asbestos mat as previously described on p. 10.

The equivalent weight of sodium hydroxide is about 40; therefore for 1 l. of 0.1 *N* solution, 4 g. is needed. However, because of the superficial coating of sodium carbonate on the hydroxide and the hygroscopicity of the base, 4.5 g. of the highest grade sticks or pellets of sodium hydroxide

[1] Instead of paraffin wax one may use Thermoprene, No. 1023, a rubber paint sold by B. F. Goodrich Co., Akron, Ohio. See Soule, *Ind. Eng. Chem., Anal. Ed.*, **1**, 109 (1929).

should be weighed out using a rough balance. Furthermore, some sodium hydroxide will be lost during the filtration called for below. After weighing, transfer to a small, glass-stoppered Pyrex bottle or test tube, add about 5 ml. of water and shake until solution is complete. A cloudiness will remain; this is the sodium carbonate which precipitates out in concentrated sodium hydroxide solution. After the solution is cool filter it through the Gooch crucible, pour the clear filtrate into the liter of water in the paraffin-coated bottle and shake. If desired the bottle may be equipped with a siphon for delivery; in that case use a two-hole rubber stopper and insert a soda-lime tube to prevent entry of carbon dioxide from the air.

Relative Concentrations of the Acid and Base. Fill two burets, one with the hydrochloric acid solution and the other with the sodium hydroxide solution. Be sure to rinse each buret with three successive 8 or 10 ml. portions of the solution with which it is to be filled, transferring the solution directly from the storage bottle to the buret.

Run 30.00 ml. of the acid from the buret into a 250 ml. beaker or into a 125 ml. Erlenmeyer flask. Dilute with about 50 ml. of carbon dioxide–free water. Add a drop or two of phenolphthalein indicator. Place the beaker under the buret filled with sodium hydroxide solution and titrate until a faint pink color is obtained which persists for 30 seconds. (After reading the buret prove that carbon dioxid ecauses the pink color to fade by blowing the breath through a glass tube into the pink solution.) From the corrected volumes of acid and base calculate the ratio of the volume of acid to base. The deviation from the mean should not exceed 1 part per 1000.

Notes. Read carefully p. 125 on the use of carbon dioxide–free water. If the titration is carried out in a beaker, instead of in an Erlenmeyer flask, stirring should be done with a gentle, circular motion. Whipping the solution with a stirring rod will introduce carbon dioxide from the air.

Repeat the above experiment using either methyl orange or modified methyl orange indicator.[2]

Record the results in ink in the notebook, using some such form as suggested in Table 13.

Standardization of Hydrochloric Acid[3]

The primary standard which is used to standardize hydrochloric acid volumetrically[4] is sodium carbonate using, of course, methyl orange or

[2] Prepare modified methyl orange: 1 g. methyl orange and 1.4 g. xylene cyanole FF in 1 l. of water, or purchase already prepared from Eastman Kodak Co. (See p. 104.)

[3] Before performing this or any other laboratory experiment of this chapter, the student should review thoroughly all topics taken up in Chapter 7.

[4] Hydrochloric acid can be standardized gravimetrically by precipitating the chloride ion and weighing as AgCl. See p. 248.

Table 13

RELATIVE CONCENTRATIONS OF HCl AND NaOH

(*Phenolphthalein Indicator*)

HCl		*NaOH*		*Ratio* $\frac{HCl}{NaOH}$
Buret Reading	*True Volume**	*Buret Reading*	*True Volume**	
(1) Final 30.00	29.94	Final 30.22	30.20	
Initial 0.00	0.00	Initial 0.00	0.00	
Volume used	29.94	Volume used	30.20	0.991
(2) Final 30.00	29.94	Final 30.28	30.26	
Initial 0.00	0.00	Initial 0.00	0.00	
Volume used	29.94	Volume used	30.26	0.989
(3) Final 30.00	29.94	Final 30.26	30 24	
Initial 0.00	0.00	Initial 0.00	0.00	
Volume used	29.94	Volume used	30.24	0 990
Mean value				0.990
Deviation	0.7 part per 1000			

* The true volume is the buret reading plus the buret correction for the particular volume; see p. 71.

any other indicator changing color at a pH around a value of 4. If sodium carbonate of a reliable grade is not available it must be prepared as described here.

Preparation of Sodium Carbonate. Place about 5 g. of pure sodium bicarbonate in a porcelain or a platinum crucible and imbed the crucible to three-fourths its height in a sand bath. Insert a 360° thermometer in the sand bath alongside the crucible and heat until the temperature registers between 275° and 290° for 1 hour. At this temperature the bicarbonate undergoes the reaction

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Do not allow the temperature to exceed 300° at the most, since above that temperature sodium carbonate decomposes:

$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

and the final product would be a mixture of sodium carbonate and sodium oxide. Cool and weigh the crucible and contents, after which heat again for 20 minutes, cool and reweigh. The process of heating and weighing is continued until a constant weight is obtained. Finally transfer the pure sodium carbonate to a glass-stoppered bottle while warm and place in a desiccator.

Procedure for Standardization. It is evident (see p. 79) that, since the equivalent weight of sodium carbonate is 53, the quantity suitable for

titrating with tenth-normal acid is from 0.16 to 0.22 g. Accurately weigh three portions of about this amount of the sodium carbonate and transfer (see p. 80) to 250 ml. beakers or to Erlenmeyer flasks. Dissolve each in about 100 ml. of water, add 2 drops of methyl orange (or modified methyl orange) and titrate with the hydrochloric acid. With methyl orange indicator the titration is carried to a point where the yellow solution assumes a very faint orange color. Wash down the walls of the beaker with water from the wash bottle; if the color becomes yellow again add acid from the buret dropwise until the orange color is restored. (If the end point is accidentally overrun—i.e., if the color of the solution becomes distinctly pink—countertitrate with the sodium hydroxide solution until the faint orange color is restored. Since the relation of the acid and the base solutions has been determined, the appropriate correction for the volume of acid equivalent to the sodium carbonate may be computed.) From the weights of the sodium carbonate and the volumes of hydrochloric acid employed the number of grams of sodium carbonate equivalent to 1 l. of the acid may be calculated to four significant figures. These three results should show an average deviation not greater than 1 part per 1000. Calculate the normality of the hydrochloric acid using the method given on p. 81, equation (1). Record the data on some such form as that suggested

Table 14

STANDARDIZATION OF HCl

Buret Reading		*True Volume**	*g.* Na_2CO_3	*g.* Na_2CO_3 *per 1 ml. HCl*	*Deviation from Mean*
(1) Final	30.23	30.17			
Initial	0.00	0.00			
Volume used		30.17	0.1612	0.005343	0.000003
(2) Final	31.71	31.65			
Initial	0.02	0.02			
Volume used		31.63	0.1690	0.005343	0.000003
(3) Final	33.88	33.82			
Initial	0.01	0.01			
Volume used		33.81	0.1810	0.005353	0.000007
Mean				0.005346	0 0000043 or 0.8/1000

Normality of HCl $= \frac{5.346}{53.00} = 0.1009\ N.$

* True volume = Buret reading plus buret correction (see p. 71).

in Table 14. From the ratio of the concentrations of the hydrochloric acid and the sodium hydroxide already determined calculate also the normality of the base. (Which ratio will you employ, that obtained using phenolphthalein as the indicator, or the one using methyl orange?)

Notes. Review methods of weighing, p. 51ff., and see p. 80

Preparation of Standard Hydrochloric Acid from Constant-Boiling Acid. At a definite atmospheric pressure and a definite rate of distillation the distillate from constant-boiling hydrochloric acid has a definite composition.[5] Table 15 gives the composition of the distillate obtained at ordinary pressures when the procedure which is described below is followed.

Table 15

COMPOSITION OF CONSTANT-BOILING HYDROCHLORIC ACID

Pressure, mm. Hg	*Concentration of Distillate in % HCl by (Vacuum) Wt.*	*Air Wt. of Distillate Containing 1 Mole (Vacuum Wt.) of HCl, in g.*
770	20.197	180 107
760	20.221	180 193
750	20.245	179 979
740	20.269	179 766
730.	20.293	179 555

Procedure. Place in a 1 l. distillation flask about 750 ml. of hydrochloric acid of a density of about 1.18. Arrange a condenser in the usual manner for distillations. Distil at a rate of 3 to 4 ml. per minute until about three-fourths of the original liquid has been distilled. Reject this distillate and continue the distillation, now collecting the constant-boiling liquid in a new, dry flask. Discontinue the process when the residual liquid has diminished to 50 or 60 ml. Record the barometric pressure to the nearest millimeter during the collection of the sample.

To prepare a solution of hydrochloric acid which will be approximately 0.1 *N* from the constant-boiling solution, proceed as follows. Place about 18 ml. of the constant-boiling solution in a previously weighed glass-stoppered weighing bottle. Weigh the bottle plus acid and quantitatively transfer (see p. 9) the acid to a 1 l. volumetric flask, dilute to the mark with water within a degree or two of the temperature for which the flask was calibrated, stopper and thoroughly shake. Calculate the exact normality of the solution.

[5] Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923).

Problem. Constant-boiling hydrochloric acid, which was collected at a pressure of 745 mm., weighing 17.9962 g. is diluted to 1000.0 ml. in a volumetric flask. Calculate the normality of the solution.

Solution.
$$N = \frac{17.9962}{179.872} = 0.10005$$

Standardization of Sodium Hydroxide

As mentioned under the standardization of hydrochloric acid, the normality of the sodium hydroxide solution may be obtained from the normality of the former and the ratio of the concentrations of the two. Often, however, it is desired that the normality of the base be established through a primary, rather than a secondary, standardization. Primary standards for solutions of strong bases are plentiful in number but the three most commonly employed are potassium biphthalate, sulfamic acid and benzoic acid.

Potassium biphthalate, $C_6H_4(COOH)COOK$, has several advantages to recommend it: it does not absorb moisture readily, so that it is easily dried at 105° and can be accurately weighed, even in rainy weather; it can be obtained in very pure form; it has a high equivalent weight and it is soluble in water. The reaction

$$HC_8H_4O_4^- + OH^- \rightarrow C_8H_4O_4^= + H_2O$$

shows that the equivalent weight is the same as the molecular weight.

Sulfamic acid is a strong monobasic acid, nonhygroscopic, and it may be obtained in a pure state for standardizations.[6] It too dissolves freely in water with which it slowly reacts:

$$HSO_3NH_2 + H_2O \rightarrow NH_4HSO_4$$

However, the above reaction does not take place rapidly enough to interfere with the standardization.

Benzoic acid, C_6H_5COOH, may be obtained from the U.S. Bureau of Standards in 99.9 per cent purity. If an analytical grade of the acid is purchased it should be carefully fused in a hot air oven at a temperature below 125°; at higher temperatures charring is likely to take place. After the fusion the cake is crushed with mortar and pestle and ground to a powder. In this form it can be accurately weighed more easily than the fluffy form which it has before fusing. Since benzoic acid is so sparingly soluble in water it must be dissolved in ethyl alcohol before titrating. Because the alcohol may be slightly acidic it is necessary to run a blank when benzoic acid is used as a standard.

Procedure Using Potassium Biphthalate or Sulfamic Acid. Accurately weigh out pure, dry samples of from 0.6 to 0.8 g. of potassium

[6] G. F. Smith Chemical Co., Columbus, Ohio.

biphthalate or 0.3 to 0.4 g. of sulfamic acid. (Confirm the fact that these weights are suitable for titrating with 0.1 *N* base; see p. 79.) Transfer the samples to 250 ml. beakers or to Erlenmeyer flasks and dissolve in about 100 ml. of carbon dioxide–free water. Add the indicator, 2 drops of phenolphthalein if the biphthalate is the standard, 2 drops of phenolphthalein or any other indicator with a pH range occurring between 4 and 9 in the case of sulfamic acid. Titrate until finally 1 drop of base from the buret brings about the color change, a faint pink persisting for 30 seconds if phenolphthalein is used. Record the data in a manner similar to that suggested in Table 14 and calculate the normality of the sodium hydroxide. The deviation from the mean should be about 1 part per 1000 or less.

Notes. Read carefully p. 125 on the use of carbon dioxide–free water. Remember too that if the titration is carried out in a beaker, instead of in an Erlenmeyer flask, stirring should be done with a gentle, circular motion. Whipping the solution with a stirring rod will introduce carbon dioxide from the air. Review methods of weighing, p. 51ff., and see p. 80.

Procedure Using Benzoic Acid. Accurately weigh pure, dry samples of benzoic acid weighing about 0.4 or 0.5 g. (see p. 79). Place the watch glass containing the acid in a beaker and add 20 ml. of ethyl alcohol. Swirl until the acid completely dissolves; this may be hastened by warming a minute or two over a steam bath. Be sure that all of the benzoic acid is in solution; then add 50 ml. of carbon dioxide–free water and 2 drops of phenolphthalein. Titrate with the sodium hydroxide solution until the appearance of a faint pink color which persists for 30 seconds. A ring of benzoic acid may have been deposited on the walls of the beaker just above the level of the solution. Rotate the beaker in a slightly tilted position so as to redissolve any such benzoic acid. If the pink color fades as a result of this, add more sodium hydroxide dropwise until a faint pink which lasts at least 30 seconds is restored.

Run a blank by combining 20 ml. of alcohol and 50 ml. of carbon dioxide–free water and adding 2 drops of indicator. Subtract any volume of sodium hydroxide solution required to impart a pink color to the blank from the titration volumes in the standardization. From the net volume of hydroxide and the weight of standard calculate the normality of the sodium hydroxide solution. Results should not show a deviation from the mean greater than 1 part per 1000.

Notes. Read notes following the procedure for standardization with potassium biphthalate.

A blank must be run because ethyl alcohol often contains small amounts of acidic constituents which require some base for neutralization. Without the blank determination the calculated normality would be too low.

Analyses Using Standard Alkali

ACIDITY OF VINEGAR

The minimum acid content of vinegar is set by law. A good quality of vinegar will run about 5 per cent acetic acid by weight. Since the density of vinegar is close to unity this means that there is around 5 g. of acetic acid per 100 ml. of vinegar, or 50 g. per liter. Therefore vinegars are approximately $5\%_0$ normal, since the equivalent weight of acetic acid is about 60. It follows then that if the sample is titrated with 0.1 *N* sodium hydroxide the volume of base used will be roughly eight times that of the vinegar. Accordingly a suitable amount of vinegar will be about 5 ml. But if a volume as small as 5 ml. is measured with a pipet the relative error introduced will be quite large. For this reason it is necessary, if high accuracy is to be attained, to weigh the sample of vinegar. If a sample of about 5 g. is weighed only to the third decimal place a precision of 1 in 5000 is secured and this is better than the precision gained in reading the volume of sodium hydroxide from the buret.

Procedure. Weigh a clean, dry glass-stoppered weighing bottle to the nearest milligram. Using a dry 5 ml. pipet, or one that has been rinsed three times with the vinegar to be analyzed, transfer about 5 ml. of vinegar to the weighing bottle. Weigh the bottle plus vinegar, again to the nearest milligram. Transfer the sample quantitatively (see p. 9) to a 125 ml. Erlenmeyer flask, add 50 ml. of carbon dioxide–free water and 2 drops of phenolphthalein and titrate with standard sodium hydroxide solution until a faint pink color appears which persists for 30 seconds. Calculate the percentage by weight of acetic acid. The deviation should be under 2 parts per 1000 for duplicate runs.

Notes. Further notes are unnecessary provided those at the conclusion of the procedure for standardizations given in the preceding sections have been studied carefully.

Problem. A sample of vinegar weighing 5.082 g. is titrated with 0.1012 *N* sodium hydroxide, 42.82 ml. being required. Calculate the percentage by weight of acetic acid.

Solution. G. eq. wts. of base used = (0.04282)(0.1012). G. eq. wts. of $HC_2H_3O_2$ present must be same. The equivalent weight of $HC_2H_3O_2$ = 60.05. Therefore

$$\% \ HC_2H_3O_2 = \frac{(0.04282)(0.1012)(60.05)(100)}{5.082} = 5.12$$

ACIDITY OF OXALIC ACID

The determination of the acidity of a sample of oxalic acid typifies the analysis for total acid in a great many substances. Of course one always must bear in mind that the acid strength of the unknown determines the choice of the indicator and whether or not carbon dioxide–free water

must be used. Therefore the principles discussed in Chapter 7 should be recalled before embarking upon any acid-base titration.

Procedure. Accurately weigh about 1 g. of the sample, dissolve in a small amount of carbon dioxide–free water in a beaker and quantitatively transfer (see p. 9) to a 250 ml. volumetric flask. Dilute to the mark, stopper the flask and shake. With a 50 ml. pipet withdraw three portions and place in 125 ml. Erlenmeyer flasks. Add 2 drops of phenolphthalein and titrate with standard sodium hydroxide solution. Calculate the percentage of acid present in terms of $H_2C_2O_4.2H_2O$. The deviation from the mean for duplicate determinations should be 1 part per 1000 or less.

Notes. Instead of using aliquot portions from the single sample dissolved in the 250 ml. of solution, one may, of course, weigh out two or more samples of about 0.2 g. each. According to the above procedure any error made in weighing or dissolving and diluting to volume will obviously be proportionately transmitted to each of the aliquot portions.

TITRATION OF BORIC ACID

It has been mentioned already (see p. 121 and Fig. 21) that boric acid is a very weak acid, having an ionization constant, K_a, of 6×10^{-10}. It therefore cannot be titrated with a 0.1 N solution of sodium hydroxide, for there will be no sharp break in the titration curve, which is to say no indicator will clearly mark the end point of the titration. However, the addition of polyhydric alcohols such as glycerol, mannitol or invert sugar transforms boric acid into comparatively strong complex acids which make possible the titration with 0.1 N alkali using phenolphthalein as the indicator. Boric acid, H_3BO_3, has a molecular weight of 61.84; it reacts like a monobasic acid so that in calculating the acidity of a sample the equivalent weight is also 61.84.

Procedure. Secure a sample which may be fairly pure boric acid or a mixture of boric acid and inert material. If the sample were pure boric acid a 0.2 g. sample evidently would be a suitable quantity, but unless the approximate composition is known it is best to make a preliminary determination by weighing out roughly 0.4 g. and, ignoring the refinements of the titration, making a quick determination of the acid strength. If the result were a titration, say, of 75 ml. it is obvious that a 0.2 g. sample should be taken for careful analysis; if the result were around 10 or 15 ml. a new sample of about 1 g. would be indicated. After accurately weighing the samples, transfer to Erlenmeyer flasks and dissolve in about 50 ml. of carbon dioxide–free water. For each 10 ml. of 0.1 N boric acid present (as indicated by the preliminary titration) add 3 or 4 ml. of 50 per cent invert sugar, or 0.5 to 1 g. of mannitol, or 4 or 5 ml. of glycerol; add also 10 drops of phenolphthalein. Titrate with standard sodium hydroxide to a faint pink color. Then add another portion of 4 or 5 ml. of

invert sugar, or the equivalent of mannitol or glycerol as indicated by the above figures. The pink color probably will disappear; in this case slowly add sufficient base to restore a faint pink. Then add another 5 ml. of invert sugar (or the equivalent in mannitol or glycerol). Repeat the alternation of base and invert sugar until the color no longer fades. Calculate the percentage of boric acid in the sample. A deviation from the mean of duplicate determinations may be as high as 5 parts per 1000.

Notes. Suppose the preliminary determination required, for example, 12 ml. of 0.1 *N* base. New samples for accurate analysis some three times as large would be in order. This would mean that these samples contained the equivalent of 36 ml. of 0.1 *N* boric acid; therefore approximately 10 or 15 ml. of invert sugar should be added at the beginning of the titration. Be sure that the polyhydric alcohol which is used is neutral.

For reasons which should be obvious from previous titrations, carbon dioxide, if present, would cause high results. Therefore, the solution should be swirled instead of shaken as the titration proceeds.

Analyses Using Standard Acid

ALKALINITY OF SODA ASH

Soda ash is crude sodium carbonate and usually contains some impurities such as hydroxide, chloride, etc. Any hydroxide present contributes, of course, to the total alkalinity of the soda ash. Analysis of soda ash by titrating with standard hydrochloric acid solution therefore does not give the percentage of Na_2CO_3 but the total basic strength of the sample. The procedure is essentially the same as given for the standardization of hydrochloric acid using sodium carbonate as the standard. However, instead of weighing out samples of 0.18 to 0.2 g. it is better to start with a larger sample, dissolve and dilute to the mark in a volumetric flask and pipet out aliquot portions which will contain around 0.2 g. each. In this manner the inaccuracy resulting from the use of a small original sample and due to the heterogeneity of technical soda ash is largely avoided.

Procedure. Accurately weigh out two samples of about 1 g. each. With a sample this great a precision of 1 part per 1000 is possible by weighing only to the third decimal place. Dissolve in a small amount of water in a beaker and quantitatively transfer (see p. 9) to 250 ml. volumetric flasks. Dilute to the mark and shake. Secure four portions for titration by transferring, with a 50 ml. pipet, two aliquots from each of the two volumetric flasks to beakers or Erlenmeyer flasks. Dilute to about 100 ml. and titrate with standard hydrochloric acid using methyl orange or modified methyl orange as the indicator. Calculate the results in terms of percentage of sodium carbonate or of sodium oxide. The deviation from the mean for titrations of two portions from the same volumetric flask

should not exceed 1 part per 1000; that for all four titrations may run as high as 2 parts per 1000.

Notes. The determination of alkali present in the soda ash as hydroxide may be determined by adding barium chloride in excess to an aliquot portion of the original solution. This precipitates the carbonate as barium carbonate. The precipitate need not be filtered off (see p. 125). Titrate with standard acid and calculate the percentage of hydroxide.

DIFFERENTIAL OR DOUBLE TITRATIONS. DETERMINATION OF CARBONATE AND HYDROXIDE IN A SINGLE SAMPLE

It has been pointed out already that in the titration of carbonates the first reaction with acid is that representing the conversion of the carbonate ion into the bicarbonate ion. After the completion of this reaction the further addition of acid converts the bicarbonate ion into carbon dioxide and water. The end points for these reactions are recognized by using two indicators, phenolphthalein and methyl orange. Reread pp. 124–125 for the full explanation of the principle of double titration, and then analyze a mixture of carbonate and hydroxide as given in the following procedure.

Procedure (A). Weigh out a sample of about 2 g. of the mixture of carbonate and hydroxide to the nearest milligram and dissolve in a small amount of water in a beaker. Then transfer quantitatively (see p. 9) to a 250 ml. volumetric flask, dilute with carbon dioxide–free water to the mark and shake thoroughly. The solution, when titrated to the phenolphthalein end point, will contain sodium hydrogen carbonate which establishes a pH of about 8.4 (see p. 97). To recognize this end point prepare a color comparator by making a solution of about 0.2 g. of sodium bicarbonate in 50 ml. of water and adding 5 drops of phenolphthalein. Keep in a stoppered 125 ml. Erlenmeyer flask.

Now withdraw from the volumetric flask with a 25 ml. pipet two portions of the sample and place in 125 ml. Erlenmeyer flasks equipped with stoppers. Add 5 drops of phenolphthalein. Remove the stopper only long enough to add the standard hydrochloric acid during the titration. Titrate until the faint pink color matches that of the bicarbonate color comparator already prepared. Approach the end point by 4-drop increments of acid from the buret. Shake well after each addition of acid for a full minute before making color comparisons.[7]

When the color match has been obtained read the buret; then add 2 drops of methyl orange indicator and continue titrating with standard hydrochloric acid until the color changes from yellow to orange or to the faintest pink. The flask need not be stoppered during this second part of

[7] Simpson, *Ind. Eng. Chem.*, **16**, 709 (1924), suggests the use of a mixed indicator to detect this end point.

the titration. Read the buret again. From the two readings calculate the percentage of sodium hydroxide and sodium carbonate in the sample. (See p. 125 for illustration.) Because the phenolphthalein end point is not sharp the precision will not be high when the above procedure is followed. The deviation for duplicate analyses may run as high as 10 parts per 1000. Better results may be obtained by method (B) below.

Notes. A sample of approximately 2 g. dissolved in 250 ml. of solution would yield about 0.2 g. in a 25 ml. aliquot portion. This obviously would require roughly 35 to 50 ml. of 0.1 *N* hydrochloric acid for a sample consisting of carbonate and hydroxide. If, however, considerable inert material were present, a larger original sample would be required to assure a titration involving over 30 ml. of acid. If the procedure given above results in an inordinately low volume of acid in the titration, it may be necessary to start again with a larger sample.

In titrating to the phenolphthalein end point the flask should be kept stoppered while shaking not only to exclude atmospheric carbon dioxide, but to avoid loss of carbon dioxide coming from the reactants. Local excess of hydrochloric acid will cause the reaction, $HCO_3^- + H^+ \rightarrow H_2O + CO_2$, to take place before the desired reaction, $CO_3^= + H^+ \rightarrow HCO_3^-$, is completed. This would cause loss of carbon dioxide in an unstoppered flask and give high results for the phenolphthalein end point. Shaking in the stoppered flask will cause the carbon dioxide to redissolve and form the bicarbonate ion.

Procedure (B). Withdraw two 25 ml. aliquot portions from the volumetric flask containing the sample as secured by procedure (A) above. With one portion determine the total alkalinity according to the procedure for the standardization of hydrochloric acid on p. 133, using methyl orange. To determine the sodium hydroxide alkalinity add to the other portion an excess (probably 10 ml. or less) of 0.5 *M* barium chloride and titrate without filtering with standard hydrochloric acid using 3 drops of phenolphthalein as the indicator. Make up a blank consisting of about 0.1 g. of sodium carbonate in 50 ml. of water and the same volume of 0.5 *M* barium chloride solution as was used in the titration. Add 3 drops of phenolphthalein. The blank will probably be white at this point. Add dropwise a standard solution of sodium hydroxide from a buret until the first faint pink appears; then add 1 drop of standard hydrochloric acid which should render the blank white again. The net result of the blank determination will be a small volume of base: a correction of an equivalent volume of acid must be added to that volume of acid used in the analysis. From the data obtained in the methyl orange and phenolphthalein titrations calculate the percentages of sodium carbonate and sodium hydroxide in the sample. Duplicate determinations should check within 5 parts per 1000 from the mean.

Notes. Read the note on p. 141.

The blank consists of a precipitate of barium carbonate and an excess of barium chloride (be sure an excess of barium chloride has been used). Therefore

its reaction should be slightly acidic and a small amount of standard base must be added to obtain a faint pink color. Since the phenolphthalein end point in the analysis is from pink to white, 1 drop of standard hydrochloric acid is added after the blank has been rendered pink in order to return to white. The volume of acid corresponding to the net volume of base employed for the blank obviously must be added to the volume of acid used for the analysis. This calculation may be made since the standard acid–standard base ratio has been determined already.

Problem. A mixture containing sodium carbonate and sodium hydroxide and weighing 0.2375 g. is dissolved and titrated to the methyl orange end point with 0.0960 *N* hydrochloric acid, 47.84 ml. being required. A second sample of the same weight is dissolved and an excess of barium chloride is added. It is titrated with the 0.0960 *N* acid using phenolphthalein as the indicator, 20.22 ml. being necessary. A blank required a net volume of 0.06 ml. of 0.0970 *N* sodium hydroxide solution. Calculate the percentage of sodium carbonate and of sodium hydroxide in the mixture.

Solution. (a) Since the acid and the base are so nearly the same normality the small volume of 0.06 ml. of base for the blank is equivalent to the same volume of acid. Thus the titration to the phenolphthalein end point becomes 20.22 + 0.06 or 20.28 ml. of standard acid.

$$\text{Total alkalinity} = (0.04784)(0.0960) = 0.001593 = \text{g. eq. wts.}$$
$$\text{NaOH alkalinity} = (0.02028)(0.0960) = 0.001947 = \text{g. eq. wts.}$$
$$\text{Na}_2\text{CO}_3 \text{ alkalinity} = 0.004593 - 0.001947 = 0.002646 = \text{g. eq. wts.}$$
$$\frac{(0.002646)(53.00)(100)}{0.2375} = 59.0\%\ \text{Na}_2\text{CO}_3$$
$$\frac{(0.001947)(40.01)(100)}{0.2375} = 32.8\%\ \text{NaOH}$$

Solution. (b) The problem may be solved also as follows. Thinking now in terms of "A" and "B" ml. as was done in the example on p. 125, it is obvious that the 47.48 ml. of acid in the first titration must represent (A + B) ml. The second titration neutralizes hydroxide alone so that the 20.28 ml. of acid must represent (A − B) ml. Therefore (A + B) = 47.84 ml. of standard acid and (A − B) = 20.28 ml. of standard acid. Subtracting gives 2B = 27.56 ml. of standard acid equivalent to the Na_2CO_3.

Knowing that 27.56 ml. of 0.0960 *N* acid is equivalent to the Na_2CO_3 and that 20.28 ml. of the acid is equivalent to the NaOH, we may proceed from this point on in exactly the same manner as shown under (a) on p. 125, leading to the results: 59.0% Na_2CO_3 and 32.8% NaOH.

DETERMINATION OF NITROGEN IN ORGANIC SUBSTANCES BY KJELDAHL METHOD[8]

The determination of nitrogen by the Kjeldahl method depends in its final step upon the indirect titration of ammonia coming from the original nitrogenous substance. Amines and amides are converted into ammonium bisulfate by digestion with concentrated sulfuric acid; the organic substance thus is decomposed, the carbon and hydrogen being oxidized to

[8] For two instructive and interesting articles see Bradstreet, *Chem. Revs.*, **27**, 331 (1940); and Oesper, *J. Chem. Education*, **11**, 457 (1934).

carbon dioxide and water while the nitrogen is converted into ammonium bisulfate. The solution then is treated with a concentrated solution of sodium hydroxide and the ammonia thus liberated is distilled into a measured volume of standard acid, present in excess. Finally the excess acid is determined by titrating with a standard alkaline solution. From the amount of standard acid equivalent to the ammonia, the percentage of ammonia, or of nitrogen, in the original sample may be computed.

The Kjeldahl method is applicable to the determination of nitrogen in foods, fertilizers and the like; if the nitrogen is fixed in forms other than amines or amides, special means must be provided to convert it into ammonium salts. Modifications of the method are necessary if the material contains azo, cyanide, hydrazine, nitro, nitroso and similar groups. In such cases one may consult other works for particular methods.[9] The oxidation of the organic compounds in the sample by hot concentrated sulfuric acid is hastened by adding anhydrous sodium or potassium sulfate. This elevates the boiling point and at the higher temperature the period of time required for the digestion is reduced. Many catalysts have been used to accelerate the digestion, including, among others, mercuric oxide, cupric sulfate, selenium oxychloride and copper selenite.

Procedure. Weigh samples of between 1 and 2 g. to the nearest milligram and place in Kjeldahl flasks. (Take care that none of the sample clings to the neck of the flask. After weighing wrap the sample in a piece of filter paper and drop into the flask, or, if this method is not employed, be sure that any material sticking to the neck is washed down when the sulfuric acid is poured in. The use of filter paper is objectionable in that the digestion period is thereby prolonged due to the resistance of the paper to oxidation.) Add 10 g. of potassium sulfate, 0.3 g. of cupric selenite (or 2 g. of cupric sulfate) and 25 ml. of concentrated sulfuric acid.

(If nitrites or nitrates are present in the unknown they would be converted into nitric acid during the reaction with sulfuric acid and lost through volatilization. This may be prevented by a modified procedure in which 25 ml. of sulfuric acid containing 1 g. of salicylic acid is added. After standing a half hour with occasional shaking the nitric acid is converted into nitrated organic compounds. Then 5 g. of sodium thiosulfate is added in small portions and the solution is heated for 5 minutes. The thiosulfate reduces the nitrated compounds to corresponding amines. The solution then is cooled and 10 g. of anhydrous potassium sulfate and 0.3 g. of cupric selenite are added. From this point forward the regular procedure is followed. Omit the salicylic acid–thiosulfate treatment only if it is known that nitrites and nitrates are absent.)

Swirl the mixture. Heat gently on the Kjeldahl digestion rack which

[9] *Official and Tentative Methods of Analysis*, Association of Official Agricultural Chemists, Washington, D.C., 1945.

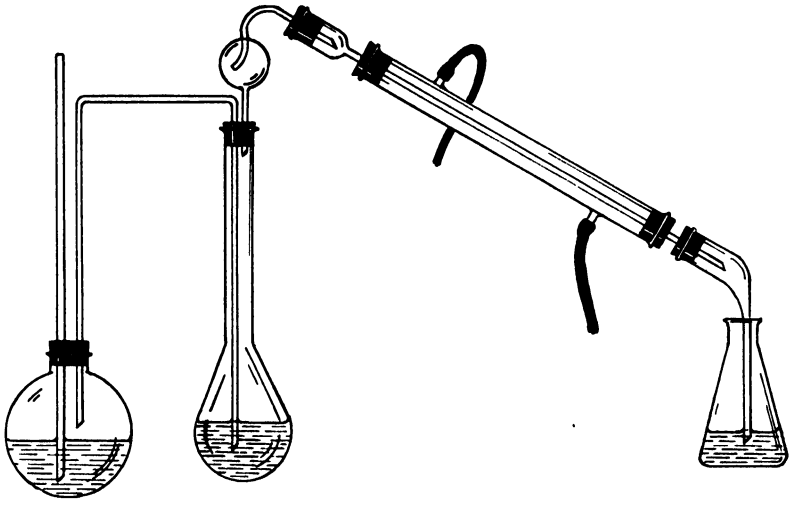


FIG. 25. Apparatus for the steam distillation of ammonia in the Kjeldahl determination of nitrogen.

provides for removal of fumes. The digestion may be carried out on the laboratory desk if a Kjeldahl rack is not available, provided an individual fume eradicator is employed.[10] When frothing ceases increase the heat to the simmering point and continue the digestion until the black solution becomes clear and light green (due to the copper of the catalyst) in color. Then digest 10 minutes longer.

Cool the flask to room temperature and carefully add 200 ml. of water. Shake and if necessary warm slightly until solution of the cake is complete. (A gelatinous precipitate will appear if any silica is present; this may be ignored.) The solution is now ready for the liberation and distillation of the ammonia.

Make ready for the distillation as follows. With a pipet place 50 ml. of standard hydrochloric acid which is about 0.1 *N* in a receiving flask marked to indicate a volume of 200 ml. Adjust the height of this flask so that the end of the adapter extends just below the level of the acid. Carry out the distillation as shown in Fig. 25, or, if equipment for a battery of distillations such as is pictured in Fig. 26 is available, this should be used; this shows a combination digestion-distillation arrangement. With the former apparatus steam distillation may be performed; this reduces the tendency toward bumping.

[10] Purchase from G. F. Smith Chemical Co., Columbus, Ohio; or prepare as recommended by Heston and Wood. Pack a Gooch crucible loosely with medium asbestos moistened with concentrated sulfuric acid. Place the crucible in the mouth of the Kjeldahl flask using lead or tin foil as a gasket to make a tight fit. The fumes are completely absorbed.

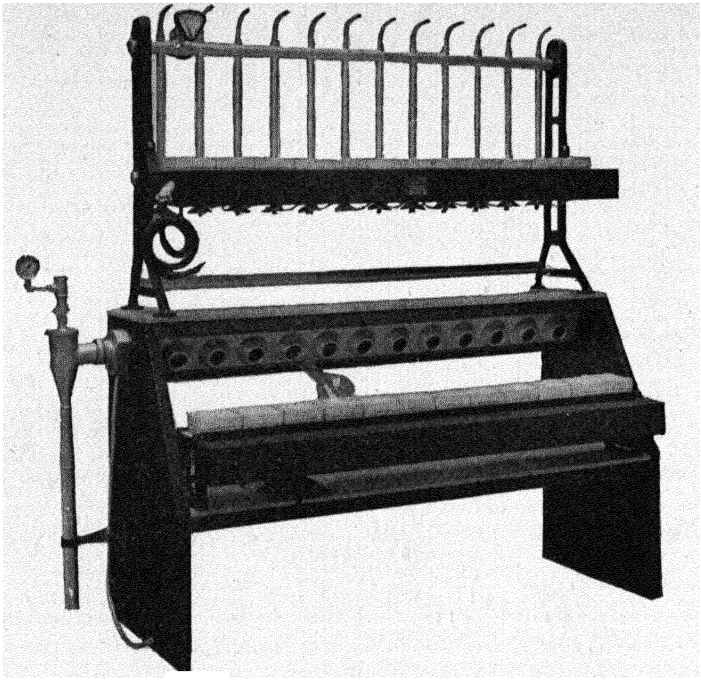


FIG. 26. Kjeldahl digestion and distillation unit. (Courtesy, E. Machlett & Son.)

Place a piece of litmus paper in the Kjeldahl flask and add 50 ml. of a cold 50 per cent solution of sodium hydroxide. (In case steam distillation is not employed add a gram of granulated zinc to prevent bumping.) In adding the sodium hydroxide solution hold the mouth of the flask away from your person so that if an unexpectedly violent reaction occurs no injury will be suffered. Swirl the flask to mix the solutions and connect at once the flask and the condenser with the Kjeldahl trap intervening. If the litmus paper is not blue at this point the solution is not basic, in which case additional base must be added.

Heat the Kjeldahl flask—with steam or directly, depending on the method of distillation—and continue to distil until the volume of liquid in the receiving flask has reached the 200 ml. level. By this time all of the ammonia will have distilled over. (In the absence of steam distillation the receiving flask should be lowered occasionally so that the end of the adapter is kept only slightly underneath the level of the liquid. If too far below the level small temperature variations could cause a suction which might draw liquid into the condenser and even into the Kjeldahl flask.) When the volume in the receiving flask reaches 200 ml. lower this flask until the adapter is no longer touching the liquid. Then turn off the steam generator (or discontinue the heating). Rinse off the adapter into the

receiving vessel and titrate the contents with a standard solution of about 0.1 *N* sodium hydroxide using 5 drops of methyl red as the indicator. From the volume of standard base used for the titration calculate how much acid must have reacted with the ammonia. Knowing the volume of acid necessary for the ammonia, and the normality of the acid, calculate the percentage of nitrogen (as such or in terms of NH_3) in the sample. The equivalent weight of nitrogen, based upon the titration of ammonium hydroxide with an acid, is of course 14.01. Duplicate results should agree within 0.3 per cent.

Notes. Both the weight of the sample and the volume of standard acid used to absorb the ammonia depend upon the nitrogen content of the sample. The instructor may indicate the approximate nitrogen content from which one may estimate suitable amounts of sample and acid. Or a single preliminary run may be made using the quantities given in the above procedure, after which, if necessary, the weight of sample and volume of acid may be varied to accommodate the needs of the particular substance to be analyzed.

The determination should be carried out in an atmosphere as free as possible from ammonia fumes, since the solution used in the analysis may absorb the fumes and cause high results.

For highest accuracy a blank should be run, for example, on a 1 g. sample of sugar, exactly as outlined for the analysis. This will correct not only for nitrogenous substances possibly present in the reagents but also for the "normal" ammonia content in the laboratory atmosphere. Subtract the volume of standard acid neutralized by ammonia in the blank from the volume of standard acid neutralized by ammonia in the analysis. The difference is the acid actually equivalent to the ammonia in the sample.

The time required for the digestion may vary from a few minutes to an hour or more depending on the substance analyzed. If the contents of the flask are not clear after an hour, turn off the heat, wait a minute (do not allow the acid in the absorbing vessel to suck back into the condenser), then quickly introduce more potassium sulfate into the Kjeldahl flask.

A very small piece of paraffin may be added to the distilling flask to reduce frothing.

When the analysis has been completed and after the contents of the Kjeldahl flask have cooled somewhat, but while still liquid, empty the flask into the sink half full of water. If the residue solidifies in the flask it may cause the flask to crack. Always steam out the condenser after finishing an analysis by running steam from boiling water through the condenser without any running water in the jacket. It is safest to steam out a condenser also just before beginning an analysis.

Boric acid may be used instead of standard hydrochloric acid to absorb the liberated ammonia.[11] The exact concentration of the boric acid solution need not be known because the ammonium borate so formed can be titrated directly with a standard acid solution, using methyl red or bromcresol green as the indicator. In this procedure the only change from that already described is the substituting of 50 ml. of 0.6 *M* boric acid (practically saturated) solution for the standard

[11] See Winkler, *Z. angew. Chem.*, **26**, 231 (1913); Meeker and Wagner, *Ind. Eng. Chem., Anal. Ed.*, **5**, 396 (1933); Wagner, *ibid.*, **12**, 771 (1940).

hydrochloric acid used to absorb the ammonia, and the final titration with standard hydrochloric acid. The end point is reached using bromcresol green when the solution assumes a faint yellow color.

Other Applications of Kjeldahl Method. Inorganic Nitrites or Nitrates. Dissolve accurately weighed samples of about 0.2 g. in 100 ml. of water. Quickly add 50 ml. of 50 per cent sodium hydroxide and 3 g. of an alloy of aluminum, copper and zinc, called Devarda's alloy. After the reaction, in which the nitrite or nitrate is reduced to ammonia, has continued for 5 minutes, start the distillation and carry on the procedure in the usual manner until two-thirds of the liquid has distilled over. Titration of the excess acid in the receiving flask with standard base using methyl red as the indicator reveals the quantity of acid equivalent to the ammonia, from which the percentage of nitrite or nitrate may be calculated. (Absorption of the ammonia in boric acid may be employed if preferred; see the final paragraph in the above section.)

Ammonium salts, analyzed according to the Kjeldahl procedure, simply may be dissolved in water, treated with an excess of sodium hydroxide and the ammonia distilled over into a measured excess of standard acid. Obviously no digestion or reduction is necessary if no organic matter is present and the nitrogen is initially in the form of ammonium ion.

Place an accurately weighed sample of 0.2 or 0.3 g. of the salt in the Kjeldahl flask. Dissolve in 100 ml. of water. After connecting the receiving flask containing 50 ml. of standard hydrochloric acid, about 0.1 *N*, quickly pour 50 ml. of 50 per cent sodium hydroxide into the Kjeldahl flask, connect the flask to the condenser, swirl to mix the contents and proceed with the distillation until two-thirds of the liquid in the flask has distilled over. Titrate the excess acid as usual, using methyl red indicator, and calculate the percentage of ammonia present. (Absorption of the ammonia in boric acid may be employed if desired; see final note p. 147.)

Questions and Problems

(See also problems at end of Chapters 6 and 7)

1. Explain why the use of the smallest quantity of an indicator that will unmistakably reveal the end point of a titration is better than a larger amount.
2. Explain the difference in the information given by a statement of the pH of a solution of an acid or a base, and a statement of the normality of the acid or base.
3. Explain the difference between the stoichiometric point and the end point of a titration. From a practical standpoint why is it that the two seldom exactly coincide?
4. In the titrations of acids and bases of various strengths against one another what calculation is involved for forecasting in a given case just what indicator will detect the end point satisfactorily? What data is needed to make such calculations?

5. Explain why any of several indicators may be employed to reveal the end point in the titration of a strong acid against a strong base when both the acid and the base are about 0.1 *N*. Explain why fewer indicators, if any, are available which will disclose the end point in such a titration if the acid and the base are used in 0.01 *N* or in 0.001 *N* concentrations.
6. A bottle of concentrated hydrochloric acid has been labeled by the manufacturer as containing 36 per cent hydrogen chloride by weight. Outline a method of analysis by which the statement may be checked. Include estimates of a suitable quantity of sample, the concentration of reagent used and the precision with which measurements and calculations should be made.
7. Explain fully why in the analysis of vinegar the sample should be weighed instead of measured volumetrically.
8. Show explicitly and concisely just when, in acid-base titrations, carbon dioxide–free water must be used, and how in certain cases the presence of carbon dioxide will cause no difficulty.
9. When carbonate and hydroxide in a mixture of the two are analyzed by the double-titration method, without precipitating the carbonate as barium carbonate, there are two reasons, both concerned with carbon dioxide, why the titration flask should be unstoppered only long enough to add the successive increments of titrating acid. Explain why this is true.
10. Whereas it is possible to have a dry mixture of sodium hydroxide and sodium bicarbonate, these two substances in the presence of moisture, or in solution, are said to be incompatible. Explain.
11. Suppose that an unknown solution contains either sodium hydroxide, sodium-bicarbonate, sodium carbonate or either of the two compatible combinations. Let A represent the volume of standard acid required to titrate the cold solution to the phenolphthalein end point, and B represent the additional volume of acid necessary to reach the methyl orange end point in a simple double titration. Explain why the information listed in the first two columns in the following table qualitatively identifies the component or components as listed in the third column.

Volume Acid to Phenolphthalein End Point	*Additional Acid to Methyl Orange End Point*	*Ions Present*
A	*0*	OH^-
0	*B*	HCO_3^-
A	$B(= A)$	$CO_3^=$
A	$B(< A)$	$CO_3^= + OH^-$
A	$B(> A)$	$CO_3^= + HCO_3^-$

12. Discuss two advantages, one of a practical nature (time saving) and one which leads to greater precision, in the analysis for nitrogen by the Kjeldahl method, if boric acid solution is used to absorb the ammonia instead of a standard acid solution.
13. Criticize the statement: the object of any acid-base titration is to neutralize the solution in the beaker.

14. A certain solution contains 0.0987 gram equivalent weight of an acid in 987 ml. of solution. What is its normality?

15. A solution of nitric acid has a specific gravity of 1.20 and contains 32.3 per cent HNO_3 by weight. Calculate its approximate normality.
Answer: 6.14 *N*.

16. Given exactly 500.0 ml. of 1.000 *N* acid. To what volume must it be diluted with 0.2000 *N* acid in order that the resulting solution will be 0.4500 *N*?
Answer: 1600 ml.

17. A solution is prepared by dissolving together 5.000 g. each of sodium hydroxide and potassium hydroxide. How many ml. of hydrochloric acid, 1.000 ml. of which is equivalent to 0.01212 g. of benzoic acid, will be necessary to neutralize the basic solution?
Answer: 2159 ml.

18. One hundred ml. of a solution of 0.2500 *N* potassium hydroxide is placed in a 250 ml. volumetric flask and brought up to the mark with a second potassium hydroxide solution. The resulting normality is found to be 0.2000 *N*. What was the normality of the second potassium hydroxide solution?
Answer: 0.1667 *N*.

19. Constant-boiling hydrochloric acid which was distilled at a pressure of 755 mm. and weighing 18.0206 g. is diluted to 1000 ml. Calculate the normality of the solution.
Answer: 0.1001 *N*.

20. A sample of pure benzoic acid weighing 0.4026 g. is titrated with a sodium hydroxide solution, 34.78 ml. being required. Calculate the normality of the alkaline solution.
Answer: 0.0948 *N*.

21. Fifty ml. of the sodium hydroxide solution of (20) is equivalent to how many grams of pure potassium biphthalate?
Answer: 0.968 g.

22. An analyst has prepared a solution of hydrochloric acid and one of sodium hydroxide. He finds that 1.000 ml. of the acid is equivalent to 0.992 ml. of the base. A sample of pure sodium carbonate weighing 0.1600 g. is dissolved in water and 45.11 ml. of the hydrochloric acid is added. The resulting solution is acidic. Upon titrating it with the sodium hydroxide solution 14.80 ml. is required. Calculate the normality of the hydrochloric acid and of the sodium hydroxide.
Answer: HCl, 0.1000 *N*; NaOH, 0.1008 *N*.

23. A sample weighing 1.058 g. contains sodium hydroxide, sodium carbonate and inert material. It is dissolved and titrated with 0.4800 *N* hydrochloric acid. Using phenolphthalein as the indicator, 28.50 ml. of the acid has been added when the color changes. Methyl orange is then added and an additional 10.52 ml. of the acid is necessary to reach the second end point. Calculate the percentage of NaOH and Na_2CO_3 in the sample.
Answer: 32.6% NaOH; 50.6% Na_2CO_3.

24. Four samples all weighing exactly 1 g. are known to be either binary mixtures of sodium carbonate, sodium hydroxide and sodium bicarbonate, plus inert material, or to consist of just one of the active ingredients and inert material. From the data below state what active component or components are pres-

ent and calculate the percentage of each. The titrating acid was 0.4800 *N* hydrochloric.

Sample	*Ml. Acid to Phenolphthalein End Point*	*Additional ml. Acid to Methyl Orange End Point*
1.....	12.08	12.08
2.....	0.00	20.20
3.....	10.04	16.61
4.	The fourth sample required 40.00 ml. of acid to reach the phenolphthalein end point; then 10.50 ml. excess acid was added and the solution was boiled. Following this the solution was cooled in an atmosphere free from carbon dioxide and titrated with 0.2400 *N* sodium hydroxide solution, 21.00 ml. being required.	

Answer: (1) 61.5% Na_2CO_3; (2) 81.5% $NaHCO_3$; (3) 51.1% Na_2CO_3 and 26.5% $NaHCO_3$; (4) 76.8% NaOH.

25. What must be the normality of the hydrochloric acid used to determine the percentage purity of soda ash (crude sodium carbonate) if exactly 1 g. samples are used, in order that the buret reading will be equal to the percentage of Na_2CO_3?

Answer: 0.1887 *N*.

26. (a) A mixture consists of pure sodium carbonate and pure barium carbonate. If 0.2500 g. of it requires 32.84 ml. of 0.1000 *N* acid for complete neutralization, what percentage of each component is present in the mixture? (b) If a 0.2500 g. sample of the same mixture is titrated to the phenolphthalein end point, how many ml. of the 0.1000 *N* acid will be required?

Answer: (a) 34.4% Na_2CO_3 and 65.6% $BaCO_3$; (b) 16.23 ml.

27. The nitrogen in a sample of food weighing 2.045 g. is determined by the Kjeldahl method. The liberated ammonia is received in 50.00 ml. of acid and the excess acid is titrated with 18.24 ml. of 0.5062 *N* sodium hydroxide solution. When 50.00 ml. of the acid is titrated directly against the base 40.00 ml. is necessary. Calculate the percentage of nitrogen in the sample.

Answer: 7.38%.

28. Find the equivalent weight of an acid 1.565 g. of which neutralize 35.58 ml. of potassium hydroxide solution, 10.00 ml. of the latter being equivalent to 0.5000 g. of pure calcium carbonate.

Answer: 44.02.

Chapter 9

OXIDATION AND REDUCTION I. STOICHIOMETRIC RELATIONS AND CALCULATIONS

OXIDATION is defined as the loss of one or more electrons by an atom or an ion; reduction is the reverse, or the gain of one or more electrons by an atom or an ion. Neither can occur in the absence of the other; that is to say, if an atom or ion is oxidized there must be another atom or ion simultaneously reduced. The atom or ion which gains electrons and itself is reduced causes another atom or ion to lose electrons; the former is therefore called the oxidizing agent or oxidant, and the latter is known as the reducing agent or reductant.

Not all oxidation-reduction reactions are suitable for application to quantitative analysis. All such reactions are reversible and unless the equilibrium point lies far to one side or the other the reaction would not be feasible as a basis for analysis. However, there are so many oxidation-reduction reactions which for all practical purposes are complete that this type of reaction finds greater application than any other in volumetric analyses.

Some oxidizing agents have a more pronounced tendency to gain electrons than others, and some reducing agents have a stronger tendency to lose electrons than others. Thus all oxidizing agents and all reducing agents reveal, under a given set of conditions, a definite electron affinity. The best oxidizing agents are those which exhibit the highest electron affinity, and the best reducing agents are those which show the lowest electron affinity. When a good oxidizing agent reacts with a good reducing agent the reaction almost attains completeness, since one reagent possesses a very high electron affinity and the other a very low electron affinity. On the other hand when the electron affinities of the oxidant and the reductant are not widely different the reversibility of the reaction between them will be revealed by the presence of considerable quantities of each after equilibrium has been attained. Obviously it is necessary that we know something of a quantitative nature about electron affinities if we are to deal in a sure and definite manner with reactions of this type. This we may accomplish through consideration of electrode potentials taken up in Chapter 10. For the moment, however, let us confine ourselves to typical oxidation-reduction reactions which commonly are used in

quantitative determinations, and take up the questions of the equivalent weight, normality, stoichiometric relations in general for such reagents, and the method of balancing the equations involved.

Equivalent Weight of Oxidizing and of Reducing Agents. It will be remembered that the gram equivalent weight of an acid, a base or a salt is that weight of the compound necessary to provide 1 gram atomic weight of replaceable hydrogen or its equivalent. The gram equivalent weight of an oxidizing agent or of a reducing agent is that weight of the compound necessary to oxidize 1 gram atomic weight of hydrogen or to reduce 1 gram atomic weight of hydrogen ion. The oxidation of one atom of hydrogen or the reduction of one hydrogen ion involves a transfer of one electron. Accordingly, the equivalent weight of an oxidizing agent or of a reducing agent is the molecular weight of the compound divided by the number of electrons lost or gained by the molecule.

It sometimes is found that a given oxidant, for example, may undergo reduction to different extents, depending upon the conditions of the reaction. For example, the permanganate ion of potassium permanganate, employed as an oxidant in an acidic solution, is converted to manganous ion with a valence of 2^+, whereas in a neutral or basic solution it is converted into manganese dioxide in which the manganese has a valence of 4^+. Obviously the number of electrons gained in the two cases is different and thus the equivalent weight of potassium permanganate is different depending upon the acidity or basicity of the solution. Again nitric acid, if used as an oxidant in concentrated solution, will be reduced to nitrogen dioxide, but used as a dilute solution it is reduced to nitric oxide or even to ammonia. The equivalent weight of nitric acid therefore varies according to its concentration in the solution used. Evidently then it is imperative that one consider the particular reaction which the reagent is undergoing, thus learning exactly how many electrons per molecule are involved, before deciding what is the equivalent weight. The knowledge of what products will result when a certain oxidation-reduction reaction takes place comes with actual experience or may be had from the literature, i.e., from the experience of someone else. For convenience a list of the more common oxidizing agents employed in quantitative work is given in Table 16, together with the product which they yield under specified conditions.

The gain or loss of electrons by an oxidant or a reductant is ascertained by noting the change in oxidation number of the atom or ion which undergoes an electron shift. For example, in $KMnO_4$ the potassium is regarded as having a valence number of 1^+ and the oxygen 2^-. The product of the number of these atoms and their valence numbers gives the total electrical charge to be attributed to potassium and oxygen, and the algebraic difference between these products must represent the total

Table 16

SOME COMMON OXIDIZING AGENTS

Agent	*Chief Product*	*Conditions*
MnO_4^-	Mn^{++}	Acidic solution
MnO_4^-	MnO_2	Neutral or basic solution
Ce^{++++}	Ce^{+++}	Acidic solution
$Cr_2O_7^-$	Cr^{+++}	Acidic solution
BrO_3^-	Br^-	Acidic solution
ClO_3^-	Cl^-	Acidic solution
PbO_2	Pb^{++}	Acidic solution
MnO_2	Mn^{++}	Acidic solution
Cu^{++}	Cu^+	Reaction with I^-
H_2O_2	H_2O	
Cl_2	Cl^-	

electrical charge for manganese since the whole molecule is electrically neutral. This is more briefly expressed as follows:

$$\begin{matrix} 1^+ & (7^+) & 8^- \\ K & Mn & O_4 \end{matrix}$$

The manganese carries a charge of 7^+ and the oxidation number of the manganese in potassium permanganate is 7^+. In the case of potassium dichromate we have:

$$\begin{matrix} 2^+ & (12^+) & 14^- \\ K_2 & Cr_2 & O_7 \end{matrix}$$

The chromium here carries a total charge of 12^+ and, since there are two atoms present in the molecule, the oxidation number of chromium is 6^+.

Thus, if potassium permanganate takes part in a reaction in which the manganese is reduced to Mn^{++} the number of electrons gained (i.e., the total change in oxidation number) is 5. It follows that the gram equivalent weight of potassium permanganate is $KMnO_4/5 = 31.61$ g. In the same manner it is evident that the gram equivalent weight of this oxidant, when used in a basic solution where MnO_2 is the product, is $KMnO_4/3 = 52.68$ g. since the electron shift is 3 electrons per molecule of oxidant. In the case of potassium dichromate the oxidation number of the chromium is 6^+ and, after reduction, the chromium is in a valence state of 3^+; thus the change in oxidation number is 3 per atom of chromium or 6 per molecule of potassium dichromate. The gram equivalent weight therefore is $K_2Cr_2O_7/6 = 49.04$ g.

When sodium oxalate reacts as a reducing agent one of the products is

carbon dioxide. The change in oxidation number for each carbon must be 1. It is evident that the total charge on the two carbons is 6^+

$$\begin{matrix} 2^+ & (6^+) & 8^- \\ Na_2 & C_2 & O_4 \end{matrix}$$

and the oxidation number for carbon in oxalates is 3^+. In CO_2 the valence of carbon is 4^+; thus per atom of carbon the electron shift is 1, and per molecule of sodium oxalate it is 2. The gram equivalent weight thus is $Na_2C_2O_4/2 = 67.01$ g. Similarly sodium thiosulfate, $Na_2S_2O_3$, when it acts as a reductant and itself is converted into sodium tetrathionate, $Na_2S_4O_6$, must have a gram equivalent weight of $Na_2S_2O_3/1 = 158.1$ g., as may be seen from the following:

$$\begin{matrix} 2^+ & (4^+) & 6^- & & 2^+ & (10^+) & 12^- \\ 2Na_2 & S_2 & O_3 & \rightarrow & Na_2 & S_4 & O_6 \end{matrix}$$

The sulfur may be regarded as having an oxidation number in thiosulfate of 2^+ and in tetrathionate of $2\frac{1}{2}^+$ (i.e., $10^+ \div 4$); the two sulfur atoms in one molecule of sodium thiosulfate therefore undergo a loss of one electron and the molecular weight and the equivalent weight are the same.

Standard Solutions of Oxidants and Reductants. Direct and Indirect Analyses. The normal solution of an oxidizing or of a reducing agent is, of course, one a liter of which contains 1 gram equivalent weight of the solute. As a rule standard solutions are made up in concentrations of about 0.1 *N*, though frequently solutions of somewhat higher or lower concentrations are used. Standard solutions are sometimes prepared by accurately weighing the oxidant or reductant, dissolving and diluting to the proper volume in a calibrated flask. Such a procedure requires that the substance be obtainable in a perfectly pure state. Potassium dichromate, potassium bromate and potassium bi-iodate, $KIO_3.HIO_3$, are examples. More often the reagents are weighed in roughly correct amounts and after dissolving in the approximately correct quantity of water the solutions are standardized by titrating against a carefully weighed standard substance. Thus a potassium permanganate solution is prepared in, say, roughly 0.1 *N* concentration, and after it has stood for several days it is filtered and then may be standardized against a suitable quantity of accurately weighed sodium oxalate. In all cases, of course, it is necessary that the criteria for standards mentioned in connection with acidimetry (p. 78) be met.

It is frequently the case that during a given standardization the titrating solution reacts directly with the substance acting as the standard. Such is true when permanganate solution reacts with oxalate, the latter

being the standard. In other instances the standard employed reacts with a second substance, added in excess, and the product of this reaction in turn reacts with the solution to be standardized. For example, we may choose potassium bromate as the standard for obtaining the normality of a solution of sodium thiosulfate. A suitable amount of potassium bromate is weighed out accurately, then dissolved and acidified, and an excess of potassium iodide is added. This results in the liberation of a quantity of iodine equivalent to the weight of the bromate. The iodine set free then is titrated with the thiosulfate solution and the volume of thiosulfate necessary is equivalent to the weight of potassium bromate used as the standard.

As was true in calculating the normality of acids and bases, so also here, the normality of a solution of an oxidizing or of a reducing agent is always equal to the grams of standard equivalent to a liter of the unknown solution divided by the equivalent weight of the standard. It is useless, let it be emphasized, in calculating the normality of a thiosulfate solution, to compute the weight of iodine liberated from the potassium iodide by the bromate. (See the section on oxidation-reduction calculations, pp. 159–163.)

By no means are all oxidizing and reducing substances suitable for the preparation of standard solutions to be used in volumetric analyses. Only those are useful which may be standardized with high accuracy and which maintain a constant normality for a reasonable length of time. The most commonly used standard oxidizing solutions are those of permanganate, dichromate, ceric and bromate ions. Thiosulfate, arsenite and oxalate are widely used as standard reducing solutions.

Analyses involving oxidation-reduction may be made either by direct or by indirect methods. If a sample for analysis is brought into solution and titrated at once with a solution of known normality we say that a direct method has been used. Thus an iron ore may be dissolved, treated so as to bring all of the iron into the ferrous state, and titrated at once with a standard permanganate or ceric solution. The indirect approach is employed if the substance being analyzed is treated with a reagent in far greater quantity than stoichiometrically necessary. In the reaction which results it is necessary that either (a) a substance be liberated which may be determined by titration, or (b) the excess of the reagent added may be determined. The latter may be illustrated by the analysis of an ore containing manganese dioxide. An excess of oxalate is accurately weighed and added to a solution of the ore and the amount of oxalate "unneeded" is determined by titrating with a standard oxidizing solution like permanganate. The difference between the total weight of oxalate and the weight of the oxalate which reacted with the permanganate is, of course, equivalent to the manganese dioxide.

Balancing Oxidation-Reduction Equations

In order to balance an equation of an oxidation-reduction reaction it is necessary, first of all, to know what are the reactants and what are the products. The former presents no difficulty since we know what substances are being brought together. If the products are unknown they must be ascertained either by referring to some reference book or by actual experiment. The chief products of the oxidizing agents listed in Table 16 are given in the second column of that table. The principal products of some reducing agents have already been mentioned, viz., oxalates yield carbon dioxide, thiosulfates yield tetrathionates. In addition, it may be mentioned that iodides, chlorides and bromides usually are converted into the corresponding halogen in analytical determinations; the products formed with other reducing agents are given in connection with the experiments in which they occur.

To illustrate: consider the oxidation of oxalic acid by potassium permanganate in the presence of sulfuric acid. The reactants are simply these three compounds. As for the products, we know that in an acidic solution permanganate is reduced to the manganous ion, Mn^{++}, and that oxalates are converted by oxidation into carbon dioxide. Thus, at once, we may write

$$KMnO_4 + H_2C_2O_4 + H_2SO_4 = Mn^{++} + CO_2 + K^+ + H^+$$

If we wish to write a molecular (instead of a simple ionic) equation we must conclude that the metallic substances on the right have to appear as sulfates since (aside from the oxidant and the reductant) that is the only cation among the reactants.[1] Thus the molecular, skeleton equation becomes

$$KMnO_4 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + CO_2 + K_2SO_4 + H_2O$$

Water is one of the products, of course; this is generally true if hydrogen ions are in contact with an oxidant.

After establishing the skeleton equation we may fix the coefficients of the oxidant and the reductant, and of their products on the right, by noting the gain and loss of electrons. We have seen already that the oxidation numbers of manganese in permanganate and carbon in oxalate are 7^+ and 3^+ respectively, and that the valence of manganese and of carbon as they appear after reacting (as seen on the right-hand side of the equation) are 2^+ and 4^+ respectively. That is to say, permanganate tends to gain 5 electrons per atom of manganese and oxalate tends to lose 1 electron per atom of carbon. But, whereas permanganate contains only one

[1] Conceivably the potassium and the manganese could occur as products in the form of their oxides. However, practically all oxides react with nearly all acids to form the corresponding salts, so that the oxides cannot appear as products in the equation.

atom of manganese, oxalate contains two atoms of carbon. Therefore each molecule of permanganate tends to gain 5 electrons but each molecule of oxalate tends to lose 2 electrons. It follows then that to secure equal numbers of electrons for both gain and loss we must use two molecules of permanganate and five molecules of oxalate.

This may be diagramed more briefly as follows:

use

$$2\ (Mn^{7+} + 5e \rightarrow Mn^{2+})$$
$$5\ (2C^{3+} - 2e \rightarrow 2C^{4+})$$

Note that these electron equations direct us (in order to have an equal gain and loss of electrons) to use 2 atoms of manganese (thus 2 molecules of permanganate) and $5 \times 2 = 10$ atoms of carbon (thus 5 molecules of oxalate).

Knowing this we also see that we must obtain, on the right, 10 molecules of carbon dioxide and 2 of manganous sulfate. Therefore

$$2KMnO_4 + 5H_2C_2O_4 + ?H_2SO_4 = 2MnSO_4 + 10CO_2 + ?K_2SO_4 + ?H_2O$$

In other words we definitely fix four coefficients when we study the gain and loss of electrons. To complete the balancing of the equation it is only necessary to note that since there are now 2 of potassium on the left we must place the figure 1 in front of K_2SO_4 on the right. The total number of sulfates on the right then becomes 3, so that the figure 3 must be the coefficient of H_2SO_4 on the left. Usually it is best to leave the coefficient of H_2O to the very last. Here, since there are 10 hydrogens from $5H_2C_2O_4$ plus 6 hydrogens from $3H_2SO_4$, the coefficient for H_2O obviously must be 8. We now have the completely balanced equation:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$$

Actually, of course, the reaction is between ions and not molecules, so that ionic equations are generally preferred. For the reaction just considered the balancing of the ionic equation consists simply in first writing the partial equations for the two systems, oxidant and reductant, so that both partial equations involve that number of electrons represented by the change in oxidation number of each:

(1) $$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$$

(2) $$C_2O_4^{=} - 2e \rightarrow 2CO_2$$

Since the lowest common multiple of 5 and 2 is 10, equation (1) must be multiplied by 2 and equation (2) by 5, yielding

$$2MnO_4^- + 16H^+ + 10e \rightarrow 2Mn^{++} + 8H_2O$$
$$5C_2O_4^{=} - 10e \rightarrow 10CO_2$$

Canceling out the $+10e$ and $-10e$ and adding gives the final, balanced ionic equation, or

$$2MnO_4^- + 5C_2O_4^= + 16H^+ = 2Mn^{++} + 10CO_2 + 8H_2O$$

Oxidation-Reduction Calculations

The same principles which govern calculations of acidimetry also apply to oxidation-reduction calculations. In brief, the guiding principle is that "equivalents are equivalent to equivalents." That is to say, whenever a certain amount of an oxidizing agent reacts, an equivalent amount of a reducing agent must react. It often is not even necessary to write the equation for the essential chemical reaction (though for a full knowledge of the complete picture this is necessary) provided one already knows the equivalent weights of the essential substances. The following examples illustrate the types of calculations most often encountered.

A. Quantity of Standard Suitable for a Titration.

Problem. What weight of sodium oxalate should be weighed for standardizing a solution of potassium permanganate which is about 0.1 *N*?

Solution. Assuming that a titration volume of about 30 ml. is desired, the amount of permanganate will be (0.030)(0.1) = 0.0030 gram equivalent weight. This then also will be the quantity of oxalate needed. The equivalent weight of sodium oxalate is 134/2. Thus the weight in grams of sodium oxalate will be

$$(0.030)(0.1)(134/2) = 0.201 \text{ g.}$$

(Compare with problem on p. 79.)

B. Preparation of Standard Solutions.

Problem 1. What weight of pure potassium bromate is needed to prepare 2000 ml. of 0.05000 *N* solution?

Solution. Bromates, when they function as oxidants, are reduced to bromides; the gain of electrons therefore is 6 per bromine. Since there is only one bromine in $KBrO_3$ there will be a gain of 6 electrons per molecule. The equivalent weight thus is $KBrO_3/6 = 167.01/6 = 27.84$. This is the weight necessary to make 1 l. of 1.000 *N* solution. Therefore 2000 ml. of 0.05000 *N* solution require

$$^{2000}/_{1000}(0.05000)(27.84) = 2.784 \text{ g.}$$

Problem 2. What weight of sodium thiosulfate, $Na_2S_2O_3.5H_2O$, is needed to prepare 750 ml. of approximately 0.1 *N* solution?

Solution. If sodium thiosulfate as a reductant loses 1 electron per molecule (see p. 155), its equivalent weight is $\frac{Na_2S_2O_3.5H_2O}{1} = 248.2$. This is the weight necessary to make 1 l. of 1 *N* solution. Therefore 750 ml. of 0.1 *N* solution requires approximately

$$^{750}/_{1000}(0.1)(248) = 18.6 \text{ g.}$$

C. Calculation of Normality. (Compare calculations, p. 80, Chapter 6.)

Problem 1. A solution of potassium dichromate was standardized against iron wire, 99.50 per cent pure. The weight of wire used was 0.2025 g. If 34.28 ml. of the dichromate solution was needed for the titration, what is its normality?

Solution.

$$N = \frac{\text{g. of Standard} \simeq \text{1 l. of unknown}}{\text{eq. wt. of standard}}$$

$$= \frac{(0.2025)(0.995)\,\frac{1000}{34.28}}{55.85}$$

$$N = 0.1052$$

Problem 2. What is the normality of a ceric ammonium sulfate solution if 48.75 ml. will oxidize that weight of KHC_2O_4 which requires 25.08 ml. of 0.1492 N NaOH for neutralization?

Solution. (a) This problem may be solved by application of the formula, $N \cdot V = N' \cdot V'$ (see p. 82, Chapter 6). However, it must be remembered that KHC_2O_4, with its one replaceable hydrogen, reacts with NaOH as a monobasic acid and, as an acid, its equivalent weight is equal to its molecular weight. With ceric solutions KHC_2O_4 reacts as a reductant and gives up 2 electrons per molecule; therefore, as a reducing agent the equivalent weight of KHC_2O_4 is half of its molecular weight. It follows, therefore, that the normality of any solution of KHC_2O_4 is twice as great when used as a reductant as when used as an acid. This means, in turn, that the product of $N \cdot V$ for KHC_2O_4 is twice the product of $N \cdot V$ for NaOH, when $N \cdot V$ for the former is related to $N \cdot V$ for the ceric solution. With these points in mind we obtain

Ceric Solution	*Oxalate Solution*
$V \cdot N =$	$N' \cdot V'$
$(48.75)N =$	$2[(25.08)(0.1492)]$
$N =$	0.1535

Solution. (b) Problem C-2 may be solved in two steps as follows, first calculating the normality of the oxalate solution (assume the oxalate to be dissolved in any convenient volume of solution, say 100 ml.), and then calculating the normality of the ceric solution.

Step 1.

Oxalate Solution	*Hydroxide Solution*
$V \cdot N =$	$N' \cdot V'$
$100\ N =$	$(0.1492)(25.08)$
$N =$	0.03742, as an acid

Therefore N of oxalate as a reductant = 0.07484.

Step 2.

Ceric Solution	*Oxalate Solution*
$V \cdot N =$	$N' \cdot V'$
$(48.75)N =$	$(0.07484)(100)$
$N =$	0.1535

Solution. (c) Problem C-2 also may be solved from the standpoint of equivalent weights. That is, we may compute the number of gram equivalent weights of NaOH involved. There must be the same number of gram equivalents of oxalate when figured as an acid, or twice that number when figured as a reductant. The gram equivalents of the ceric oxidant must be the same as the gram equivalents of oxalate when the latter is figured as a reductant. Knowing the gram equivalents of ceric present per liter, we have the normality of the ceric solution.

$$\text{G. eq. wts. of NaOH} = \frac{(25.08)(0.1492)}{1000}$$

$$\text{G. eq. wts. of } KHC_2O_4 = \frac{(25.08)(0.1492)}{1000}, \text{ as acid}$$

$$\text{G. eq. wts. of } KHC_2O_4 = \frac{2(25.08)(0.1492)}{1000}, \text{ as reductant}$$

$$\text{G. eq. wts. of ceric in 48.75 ml. ceric solution} = \frac{2(25.08)(0.1492)}{1000}, \text{ as oxidant}$$

$$\text{G. eq. wts. of ceric in 1000 ml. ceric solution} = \frac{1000}{48.75} \cdot \frac{(2)(25.08)(0.1492)}{1000}$$
$$= 0.1535$$

Thus normality of ceric solution = 0.1535

D. Analyses.

Problem 1. (a) Calculate the percentage of iron in an ore if a 0.2500 g. sample, dissolved in acid and completely reduced, requires 30.32 ml. of 0.1000 *N* potassium permanganate solution for oxidation. (b) What is the "iron value" of the permanganate solution?

Solution. (a) Since 1000 ml. of 1 *N* solution contains 1 g. eq. wt., then

$$\frac{30.32}{1000}(0.1000) = 0.003032 \text{ g. eq. wt. of } KMnO_4$$
used and therefore also equals the g. eq. wts. of iron present

Then

$$(0.003032)(55.85) = \text{g. of Fe present and}$$
$$\frac{(0.003032)(55.85)(100)}{0.2500} = \% \text{ Fe} = 67.7$$

Solution. (b) The term "iron value" means the number of grams of iron which may be oxidized by 1 ml. of the oxidant. Since 1000 ml. of 1 *N* solution contains 1 g. eq. wt. it obviously is capable of oxidizing 1 g. eq. wt., or 55.85 g. of iron; 1 ml. of 1 *N* solution (of any oxidant used, whether permanganate or not) will oxidize 0.05585 g. of iron. But this solution is only 0.1000 *N* and thus its iron value is evidently 0.005585. In general, then, the metal value is

$$\frac{N}{1000} \cdot (\text{eq. wt. of constituent sought})$$

or, in the present case,

$$\frac{0.1000}{1000}(55.85) = \text{iron value} = 0.005585$$

Problem 2. Suppose we have the same data exactly as given in Problem D-1 except that, instead of the normality of the permanganate solution being given, we are told that 1 ml. of the permanganate solution is equivalent to 0.006701 g. of $Na_2C_2O_4$. What percentage of iron is present?

Solution. The problem could be solved in two steps, first by calculating the normality of the $KMnO_4$ solution, then solving as already explained. The normality of the $KMnO_4$ is

$$N = \frac{\text{g. of standard} \div \text{l l. of unknown}}{\text{eq. wt. of standard}}$$

$$N = \frac{(1000)(0.006701)}{134.0/2} = 0.1000$$

However, this problem may be more directly attacked as follows:

Since the iron present is equivalent to 30.32 ml. of permanganate it is equivalent to (30.32)(0.006700) g. of $Na_2C_2O_4$. This is equal to $\frac{(30.32)(0.006700)}{134.0/2}$ = 0.003032 g. eq. wt. of oxalate, and we have the same number of g. eq. wts. of iron present. Accordingly,

$$(0.003032)(55.85) = \text{g. of Fe present}$$

which, as already shown, equals 67.7 % Fe for the 0.2500 g. sample.

Problem 3. Calculate the percentage of iron in terms of Fe_2O_3 in an ore if a 0.2500 g. sample, dissolved in acid and completely reduced, requires 30.32 ml. of 0.1000 *N* potassium permanganate solution for oxidation.

Solution. This problem is precisely the same as D-1 except that the answer is called for in terms of iron oxide instead of metallic iron. In other words, the question is, if the iron in the ore were isolated and converted into Fe_2O_3, what percentage of the total weight of the ore would this Fe_2O_3 constitute?

Proceeding in the same manner as under solution (a) of problem D-1, we obtain

0.003032 = g. eq. wts. of $KMnO_4$ used and therefore also equals the g. eq. wts. of Fe_2O_3 present

The equivalent weight of Fe_2O_3 is the molecular weight divided by 2 since there are two atoms of iron, each of which involves 1 electron when oxidized from the ferrous to the ferric state. Then

$$(0.003032)\frac{159.7}{2} = \text{g. of } Fe_2O_3$$

$$\frac{(0.003032)(159.7/2)(100)}{0.2500} = \%\ Fe_2O_3 = 96.8$$

Problem 4. A certain oxidizing solution has an iron value of 0.005000. In the determination of iron in a 0.5000 g. sample of ore 25.00 ml. of the solution was required to oxidize the iron. What percentage of iron was in the ore?

Solution. The iron value of the oxidant is 0.005000, so that 1 ml. of the solution will oxidize 0.005000 g. of iron. Therefore

$$(25.00)(0.005000) = \text{g. of Fe present, and}$$

$$\frac{(25.00)(0.005000)(100)}{0.5000} = \%\ Fe = 25.00$$

Problem 5. One ml. of a sodium thiosulfate solution is equivalent to 0.005567 g. of pure $KBrO_3$. (a) Calculate its normality. (b) What is the copper value of the thiosulfate solution? (c) What weight of copper ore must be weighed out for analysis in order that the percentage of copper present will be identical with the buret reading?

Solution. (a) The equivalent weight of $KBrO_3$ is one-sixth of its molecular weight (see Table 16). Therefore, for the thiosulfate solution

$$N = \frac{(1000)(0.005567)}{167.0/6} = 0.2000$$

Solution. (b) From Table 16 it is seen that copper when reduced changes valence from Cu^{++} to Cu^{+}, or 1 electron is gained. Therefore, its equivalent weight is equal to its atomic weight so that for this thiosulfate solution

$$\text{Copper value} = \frac{(0.2000)(63.54)}{1000} = 0.01271$$

Solution. (c) In general, evidently

$$\% \text{ Cu} = \frac{(\text{Cu value})(\text{ml. thio.})(100)}{\text{wt. sample}}$$

Let

$$\% \text{ Cu} = X$$

Then

$$\text{ml. thio.} = X$$

Let

$$\text{wt. sample} = Y$$

Then

$$X = \frac{(0.01271)(X)(100)}{Y}$$

Canceling out X on both sides and solving for Y,

$$Y = 1.271 \text{ g. of sample.}$$

The above may appear to be a "trick" problem but it is not. In laboratories where many identical analyses are to be made much time may be saved by such an expedient as the above, since once the weight of sample to be taken is calculated, further computations are avoided.

Chapter 10

OXIDATION AND REDUCTION II. THEORY

THE STUDY of the subject of oxidation and reduction may be approached in many ways. Oxidation originally meant a gain of oxygen by a substance; later it was said to be a gain in positive valence. Again it is defined as a loss of electrons. One substance is called a good oxidizing agent because it is found by experiment to be capable of effecting the oxidation of a great many substances; another oxidant is regarded as weak because it oxidizes relatively few substances. If we are to acquire a quantitative and comprehensive understanding of oxidation it is necessary that we learn how to measure the effectiveness of an oxidant, what it may or may not do in reacting with reductants, and why, for example, a given substance behaves as an oxidant toward one compound but as a reductant toward another. Such interpretations may be developed best from the standpoint of electrode potentials.

A METAL IN CONTACT WITH A SOLUTION OF ITS IONS

When metals other than the alkalies and alkaline earths are brought into contact with water, they do not appear to dissolve. However, there is a tendency for them to do so and the slight extent to which they succeed results in the formation of a small concentration of metallic ions in the solution. Zinc, for example, when it dissolves, even slightly, undergoes the reaction

$$Zn^0 - 2e \rightarrow Zn^{++}$$

and the electrons set free accumulate on the undissolved metal, imparting to it a negative charge. This brings about a difference in electrical potential between the solution containing the positive zinc ions and the metallic zinc dipping into the solution.

Of course as soon as zinc ions enter the liquid they begin to deposit upon the zinc strip, that is,

$$Zn^{++} + 2e \rightarrow Zn^0$$

and sooner or later the rate of ionization must equal that of deposition, or

$$Zn^0 - 2e \rightleftarrows Zn^{++}$$

When the rates become equal a state of equilibrium is attained and for the equilibrium at a given temperature and pressure

$$\frac{[Zn^{++}]}{Zn^0} = k$$

Since Zn^0 is a solid its concentration is constant so that the equilibrium expression may be simplified to read

$$[Zn^{++}] = K$$

The above mathematical expression simply states that when metallic zinc is placed in contact with a solution of its ions there is one concentration, and one only, at which there is no difference in electrical potential between the solution and the metal. This is called the equilibrium concentration, and under given conditions of temperature and pressure it is characteristic for each metal.

Suppose that a piece of metal is immersed in a solution of its ions not of equilibrium concentration. The net reaction which takes place will be that which tends to establish the equilibrium concentration. Immersed in a more dilute solution of its ions the metal will send forth more ions into the solution and thus itself acquire a negative charge. If the metal is placed in a solution of its ions of greater concentration than the equilibrium value, metallic ions will deposit from the solution, and this would cause the metal to acquire a positive charge in respect to the solution. In either case a reaction takes place which tends toward the equilibrium concentration. Thus there will be a difference in electrical potential between metal and solution, and the extent of this difference will depend chiefly on two factors, namely, just what the value of the equilibrium concentration is, and the actual concentration of the ions in the solution.

It appears from what has been stated above that any metal could be charged positively (by placing it in a solution of its ions of greater than equilibrium concentration) or negatively (by placing it in a solution of its ions of less than equilibrium concentration) or even not at all (if placed in a solution of exactly equilibrium concentration). With some metals, like silver, the equilibrium concentration is of such magnitude that any of these three possibilities can be realized. In the case of zinc, however, the equilibrium concentration is so high that, due to the limit of solubility of its salts, no solution of equilibrium concentration can be made; therefore, zinc always acquires a negative charge when dipped into any solution of zinc ions.

Limited Solubility of Metals. As a matter of fact, if zinc is immersed in pure water no appreciable quantity of zinc dissolves, and when silver is placed in contact with a concentrated solution of its ions no appreciable

amount of silver ions is deposited. The explanation is that either action is brought to a standstill almost as soon as started. When zinc, for example, is placed in water it does dissolve very slightly. The zinc strip thus acquires a negative charge and, being negative, it attracts to it the very ions which donated electrons and charged the strip negatively. Thus there results an electrical double layer as sketched in Fig. 27, and the electrostatic attraction so created forestalls further solution of the zinc atoms. If additional atoms of the metal did give up electrons the ions would be pulled back by

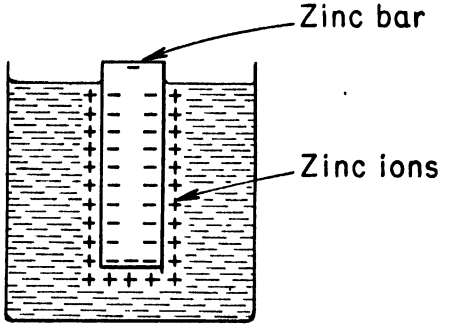


FIG. 27. Electrical double-layer between metal and solution.

the attraction of the negative strip of zinc and also would be repelled by the blanket of positive zinc ions crowding around the metal. Therefore, instead of there being two opposing forces—namely, the force tending to cause solution (called the electrical solution tension) and the force tending to cause the ions to deposit (the osmotic pressure)—we actually have the following:

$$\text{Solution tension} \rightleftarrows \text{Osmotic pressure} + \text{Electrostatic attraction}$$

Because the second factor on the right is so large it follows that the osmotic pressure may be almost zero when the opposing forces are in balance. This means that almost no ions are in solution, or that practically no metal has dissolved when the reaction reaches a stable state. Likewise, a state of balance between the opposing forces comes about before an appreciable quantity of ions are deposited upon a metal when it dips into a solution of its ions of greater than equilibrium concentration. As a consequence, when a metal is in contact with a solution of its ions, even though only the slightest quantity of metal may have dissolved (or ions deposited), there will develop a potential between the metal and the solution unless the concentration of ions in the solution is the characteristic equilibrium concentration.

SINGLE ELECTRODE POTENTIAL

The question naturally arises: What is the magnitude of the potential which exists when a given metal is in contact with a solution of its ions? The magnitude depends upon the relative tendencies of the atoms to become ions and the ions to redeposit as atoms. Under a given set of conditions—i.e., the particular metal (or any element, for that matter) and a given temperature and pressure—the electrolytic solution tension is a constant. The tendency of the ions to redeposit is proportional to the osmotic pressure and therefore to the concentration of the ions in the solution. Since the osmotic pressure depends on the concentration, it is necessary that we adopt a standard concentration before attempting to obtain a measure of a given electrode potential. The concentration of ions which has been accepted as standard is that in which the activity of the ions is unity. With this understanding the elements may be listed as in Table 17, which gives the single electrode potentials, E^0, under the standard condition of concentration and at 25°. It may be shown[1] that the Nernst equation[2] gives the relationship for the potential existing between a metal in contact with a solution of its ions. At 25° it takes the form,[3]

$$E = E^0 + \frac{0.0591}{n} \log C \tag{1}$$

where E is the electromotive force (the potential) in volts between the metal and the solution, E^0 is a constant for a given metal, n is the valence of the ion[4] and C is the concentration of the ions in the solution in moles per liter. The Nernst equation is accurate only for dilute solutions. Actually it is the activity of the ions instead of the concentration which should be employed, but the use of the latter does not greatly affect the value of E in fairly dilute solutions.

Note that when C is equal to unity (standard concentration), log C equals zero and equation (1) yields $E = E^0$. This particular value, E^0, is known therefore as the molar electrode potential. (In the older literature it has often been called the normal electrode potential.)

The single electrode potential cannot be directly measured for the simple reason that to measure a given e.m.f. (electromotive force) it is

[1] See any textbook in physical chemistry.

[2] Nernst, *Z. physik. Chem.*, 4, 129 (1889).

[3] In all calculations in this chapter involving the Nernst equation the temperature of 25° will be understood unless otherwise stated.

[4] Actually n is the difference between the valence of the metal and the ion. Since the valence of the metal itself is zero, this difference becomes the same as the valence of the ion. However, for the potential established by an ion present in two different valence states, the value of n becomes the difference between the two valences, e.g., for the system Sn^{++++}, Sn^{++} the value of n is 2. (See equation (1), p. 176.)

necessary that the current of electricity be made to flow through some electrical measuring device such as a voltmeter or a potentiometer. This necessitates a completion of the electrical circuit by passing the current from one potential, through the measuring instrument, and thence to a second metal which is in contact with the original solution, either directly or indirectly. The second metal of course has its own potential. Thus what may be done is to obtain the relative value of a given electrode potential as compared with that of another selected as the standard potential. By international agreement all electrode potentials are based upon the arbitrary assignment of zero potential to the molar hydrogen electrode.

The hydrogen electrode consists of a stream of gaseous hydrogen passing over a platinum electrode terminating in the form of a platinum foil upon which is deposited a layer of platinum black. The platinum black adsorbs the gas and presents a blanket of hydrogen atoms to the solution of hydrogen ions in which it is immersed. The electrode potential obtained with this arrangement when the hydrogen gas at a pressure of 1 atmosphere saturates a solution of hydrogen ions at a concentration (activity) of 1 *M*, is the potential arbitrarily taken as zero. (The activity of hydrogen ions is unity in a 1.2 *M* solution of hydrochloric acid; in a 1 *M* solution the activity is slightly less than 1 but, as already mentioned, the error introduced by employing a molarity of 1 instead of an activity of 1 is so small that we shall henceforth speak of molarity instead of activity.)

Measurement of Electrode Potential. Suppose that we wish to measure the electrode potential between silver and a 1 *M* solution of silver ions. We may set up a cell as shown in Fig. 28. In this cell the hydrogen electrode is called the reference electrode since the information being sought in regard to the silver electrode is obtained through measuring the e.m.f. which is developed by the silver half-cell in combination with the hydrogen half-cell. As a matter of fact hydrogen electrodes are seldom used as reference electrodes because of the great care necessary in handling them. The most popular reference electrode is the calomel electrode. (See Fig. 37 for a sketch of the calomel electrode.) However, no matter what reference electrode is used, once its own potential is established (based on the hydrogen electrode) any measurement made through its use is automatically on the basis of zero potential for the hydrogen electrode.

The cell of Fig. 28 may be designated as

$$\mathrm{Ag} \,\Big|\, \mathrm{Ag}\ (1\ M) \,\Big\|\, \begin{matrix} \mathrm{H^+}\ (1\ M) \\ \mathrm{H_2}\ (1\ \mathrm{atm.}) \end{matrix} \,\Big|\, \mathrm{Pt}$$

the silver electrode being positive. The reading on the potentiometer is the net result of four different potentials: the electrode potential of the silver electrode, the electrode potential of the hydrogen electrode and the potentials at the two junctions of the salt bridge and the solutions. The

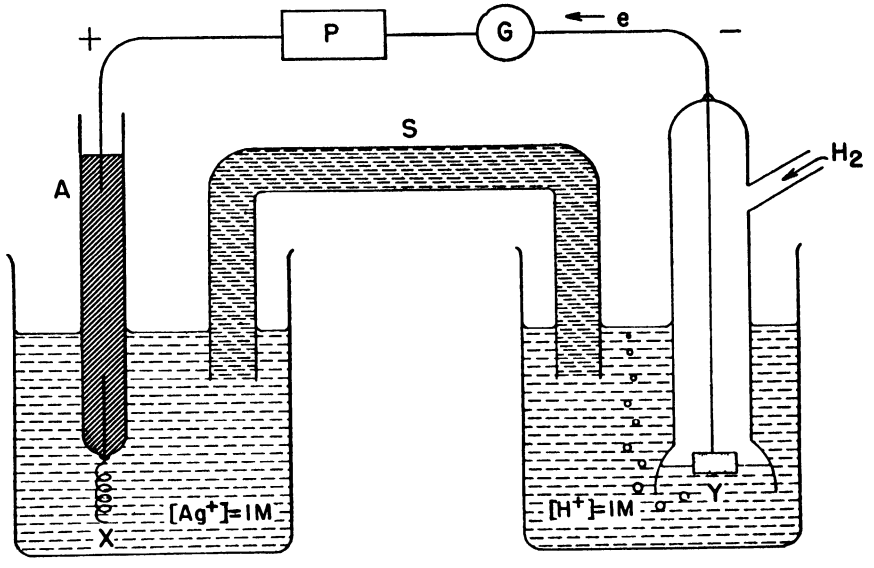


FIG. 28. Apparatus for determining E^0 for silver. (*A*) Glass tube filled with mercury. (*G*) Galvanometer. (*P*) Potentiometer. (*S*) Salt bridge (an inverted U-tube containing a salt solution, used to provide a pathway for conducting ions from one half-cell to the other). (*X*) Silver electrode. (*Y*) Hydrogen electrode.

last two potentials, known as liquid junction potentials, are so small (usually amounting only to 0.01 to 0.03 volt) that we shall regard them as negligible. The symbol $\|$ in designating a cell as above is used to indicate a salt bridge the potential effects of which are disregarded.

The e.m.f. which is registered by the potentiometer is then the difference between the potentials of the two half-cells, the silver half-cell and the hydrogen half-cell. From the Nernst equation for the former,

$$E_1 = E^0_{Ag} + 0.0591 \log [Ag^+]$$

and for the latter,

$$E_2 = E^0_H + 0.0591 \log [H^+]$$

For the cell as a whole the e.m.f. will be

$$E_{cell} = E_c = E_1 - E_2$$
$$= (E^0_{Ag} + 0.0591 \log [Ag^+]) - (E^0_H + 0.0591 \log [H^+])$$

Since the concentration of each ion is unity and E^0_H is arbitrarily assigned a value of zero, the above expression becomes

$$E_c = E_1 - E_2 = (E^0_{Ag} + 0) - (0 - 0)$$

or

$$E_c = E^0_{Ag}$$

where E_c is the e.m.f. of the cell as read from the potentiometer. In the case of silver it is found that the reading on the potentiometer is 0.80 volt, meaning that the potential between a silver electrode and a 1 *M* solution of silver ions is 0.80 volt more positive than the molar hydrogen electrode.

In a similar manner the value of E^0 for copper may be determined; the setup will be the same as described for silver except that the left half-cell consists of a copper electrode immersed in a 1 *M* solution of copper ions. The value so determined proves to be 0.34 volt. This cell is represented:

$$\mathrm{Cu} \left| \mathrm{Cu^{++}}\ (1\ M) \right\| \begin{matrix} \mathrm{H^+}\ (1\ M) \\ \mathrm{H_2}\ (1\ \mathrm{atm.}) \end{matrix} \Bigg| \mathrm{Pt}$$

Similarly the value of E^0_{Zn} may be obtained; it is found to be -0.76 volt. The zinc electrode is the negative electrode. That is to say, the molar electrode potential of zinc is 0.76 volt below that of the molar hydrogen electrode. Incidentally, from what has been stated above it follows that the cell,

$$\mathrm{Cu} \mid \mathrm{Cu^{++}}\ (1\ M) \parallel \mathrm{Zn^{++}}\ (1\ M) \mid \mathrm{Zn}$$

will yield an e.m.f. equal to

$$E_1 - E_2 = 0.34 - (-0.76) = 1.10 \text{ volts}$$

We may sum up what has been said regarding the single electrode potentials of silver, copper, hydrogen, and zinc, when measured in molar solution of their ions, as follows:

Reaction	*Oxidizing Potential (based on molar hydrogen electrode = 0)*
$Ag^+ + e = Ag^0$	0.80
$Cu^{++} + 2e = Cu^0$	0.34
$H^+ + e = \frac{1}{2}H_2^0$	0 00
$Zn^{++} + 2e = Zn^0$	−0.76

Other values are found in Table 17. Thinking of the reaction as being: (Higher Valence State) + ne = (Lower Valence State), it is the custom to give the positive sign to those electrodes which, at molar concentrations, yield potentials that are greater (more positive) than the standard (molar) hydrogen electrode, and to give the negative sign to those electrodes which yield a smaller (more negative) potential than the molar hydrogen electrode. This is another way of saying that the positive sign is given to any electrode if the electron affinity of the ion is greater than that of hydrogen ion, as is true of silver and copper cited above. Zinc ion, however, is found

Table 17

MOLAR ELECTRODE POTENTIALS AT 25°

[*(g), (l) and (s) in the table indicate that the electrode reaction takes place in a solution which is saturated with the gas, liquid or solid present in the system*]

Electrode Reaction	E^0, *in Volts*
$F_2\ (g) + 2e = 2F^-$	2.85
$Pb^{++++} + 2e = Pb^{++}$	1.69
$MnO_4^- + 4H^+ + 3e = MnO_2\ (s) + 2H_2O$	1.67
$2BrO_3^- + 12H^+ + 10e = Br_2\ (l) + 6H_2O$	1.52
$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$	1.50
$2ClO_3^- + 12H^+ + 10e = Cl_2\ (g) + 6H_2O$	1.47
$PbO_2\ (s) + 4H^+ + 2e = Pb^{++} + 2H_2O$	1.46
$Ce^{++++} + e = Ce^{+++}$ (see footnote 10, p. 199)	1.45
$ClO_3^- + 6H^+ + 6e = Cl^- + 3H_2O$	1.45
$BrO_3^- + 6H^+ + 6e = Br^- + 3H_2O$	1.44
$Cr_2O_7^- + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$	1.36
$Cl_2\ (g) + 2e = 2Cl^-$	1.36
$MnO_2\ (s) + 4H^+ + 2e = Mn^{++} + 2H_2O$	1.28
Nitro-orthophenanthroline-ferrous indicator	1.25
$O_2\ (g) + 4H^+ + 4e = 2H_2O$	1.23
$IO_3^- + 12H^+ + 10e = I_2\ (s) + 6H_2O$	1.20
Orthophenanthroline-ferrous indicator	1.14
$IO_3^- + 6H^+ + 6e = I^- + 3H_2O$	1.09
$Br_2\ (l) + 2e = 2Br^-$	1.07
$VO_2^+ + 2H^+ + e = VO^{++} + H_2O$	1.00
$2Hg^{++} + 2e = Hg_2^{++}$	0.91
$2Cu^{++} + 2I^- + 2e = Cu_2I_2\ (s)$	0.88
$Hg^{++} + 2e = Hg\ (l)$	0.85
Diphenylamine sulfonic acid indicator	0.84
$Hg_2^{++} + 2e = 2Hg\ (l)$	0.80
$Ag^+ + e = Ag\ (s)$	0.80
$Fe^{+++} + e = Fe^{++}$	0.78
Diphenylbenzidine indicator	0.76
Diphenylamine indicator	0.76
$C_6H_4O_2 + 2H^+ + 2e = H_2C_6H_4O_2$	0.70
$H_3AsO_4 + 2H^+ + 2e = HAsO_2 + 2H_2O$	0.56
$I_3^- + 2e = 3I^-$	0.54
$I_2\ (s) + 2e = 2I^-$	0.54
$Cu^+ + e = Cu\ (s)$	0.52
$Fe(CN)_6^{\equiv} + e = Fe(CN)_6^{\equiv}$	0.36
$Cu^{++} + 2e = Cu\ (s)$	0.34
$Hg_2Cl_2\ (s) + 2e = 2Hg\ (1) + 2Cl^-$ (normal calomel)	0.28
$AgCl\ (s) + e = Ag\ (s) + Cl^-$	0.22
$Cu^{++} + e = Cu^+$	0.17
$Sn^{++++} + 2e = Sn^{++}$	0.15
$S\ (s) + 2H^+ + 2e \leftarrow H_2S\ (g)$	0.14
$AgBr\ (s) + e = Ag\ (s) + r^-$	0.07
$2H^+ + 2e = H_2\ (g)$	0.00

Table 17—(Continued)

Electrode Reaction	E^0, *in Volts*
$2H^+ + 2e = H_2$ (g)	0.00
$Pb^{++} + 2e = Pb$ (s)	−0.13
$Sn^{++} + 2e = Sn$ (s)	−0.14
AgI (s) $+ e = Ag$ (s) $+ I^-$	−0.15
$V^{+++} + e = V^{++}$	−0.20
$Ni^{++} + 2e = Ni$ (s)	−0 25
$Co^{++} + 2e = Co$ (s)	−0 29
$Cd^{++} + 2e = Cd$ (s)	−0.40
$Cr^{+++} + e = Cr^{++}$	−0.41
$Fe^{++} + 2e = Fe$ (s)	−0.44
$2CO_2$ (g) $+ 2H^+ + 2e \leftarrow H_2C_2O_4$	−0.49
S (s) $+ 2e = S^=$	−0 51
$Cr^{+++} + 3e = Cr$ (s)	−0.71
$Zn^{++} + 2e = Zn$ (s)	−0.76
$2H_2O + 2e = H_2 + 2OH^-$	−0.83
$Mn^{++} + 2e = Mn$ (s)	−1.05
$Al^{+++} + 3e = Al$ (s)	−1 67
$Mg^{++} + 2e = Mg$ (s)	−2.34
$Na^+ + e = Na$ (s)	−2.71
$K^+ + e = K$ (s)	−2.92
$Li^+ + e = Li$ (s)	−3.02

to have a lesser electron affinity than hydrogen ion so that the electrode potential for zinc is negative. Still another way of looking at these facts is illustrated if we merely say that zinc has a greater tendency to give up (two) electrons (and go into solution as zinc ions) that does silver or copper.

It is obvious also that since (a) oxidation is defined as a loss of electrons, (b) an oxidizing agent itself is reduced when it functions as an oxidant, (c) high electron affinity means a strong tendency to gain electrons and (d) strong oxidizing agents therefore have a high electron affinity; then strong oxidizing agents will have large positive electrode potentials. Conversely, the strongest reducing agents will have large negative electrode potentials. These conclusions may be confirmed by consulting Table 17.

Sign of Anode and Cathode. When considering voltaic cells (which generate electrical current) and electrolytic cells (which consume electrical current), it should be borne in mind that the terms anode and cathode designate respectively the electrode at which oxidation and reduction take place. Thus in the copper-zinc voltaic cell above, since zinc goes into solution according to the reaction, $Zn^0 - 2e \rightarrow Zn^{++}$, zinc is the negative electrode. Because this reaction represents oxidation of the zinc the negative electrode is the anode. By similar reasoning it may be shown that the positive copper electrode is the cathode.

On the other hand, if an electrical current is passed from an outside source through a solution of a zinc salt at a sufficient voltage, the positive zinc ions will migrate to and deposit upon the negative electrode. The reaction, $Zn^{++} + 2e \rightarrow Zn^0$, represents reduction; thus here the negative electrode is the cathode. Whatever reaction takes place at the positive electrode proves it to be the anode.

Therefore the signs of the anode and cathode in a voltaic cell are the reverse of what they are in an electrolytic cell. To summarize: in voltaic cells the anode is negative and the cathode is positive; in electrolytic cells the anode is positive and the cathode is negative.

Standard States and Conventions

In perhaps no other phase of chemical studies has more confusion for the student developed, particularly in regard to keeping straight the matter of signs and the direction of reaction, than in electrometric measurements. It is necessary, therefore, to define carefully the conditions under which measurements are made, and the conventions which are employed. The following conditions are generally accepted.

1. The standard state for the concentration of ions is 1 *M* (strictly, activity = 1). A difficultly soluble salt is said to be at standard state when its solution is at equilibrium with undissolved solid.

2. A pure liquid or solid is automatically at standard state.

3. A gas is at standard state at a pressure of 1 atmosphere. For a gas in solution standard state is the concentration of the dissolved gas which is in equilibrium with the gaseous phase when the latter is at a pressure of 1 atmosphere.

4. The activity of a solid or liquid not in a pure state is the mole fraction, i.e., moles of component divided by total moles present. Thus in dilute aqueous solutions the mole fraction of water is practically unity and its activity is 1. In the case of a gaseous solution ("mixture") the activity is the partial pressure in atmospheres.

5. Reactions taking place in the two half-cells are written as given in Table 17 and not the reverse.

6. In representing the cell the electrode which has the more positive molar potential is written on the left side. (See e.g., the copper-zinc cell, p. 170.) In writing the equation for the chemical reaction taking place the substance in the left half-cell appears in its higher valence state on the left side in the chemical equation. (For example, note the designation of the copper-zinc cell, p. 170; the chemical reaction is written: $Cu^{++} + Zn^0 = Cu^0 + Zn^{++}$.)

7. In obtaining the e.m.f. of a given cell the potential of the right electrode is subtracted from that of the left electrode; i.e., $E_c = E_1 - E_2$.

8. A positive e.m.f. for the cell means that the electrons in the external circuit flow from right to left and the chemical reaction will go spontaneously from left to right. A negative e.m.f. for the cell means that the flow

of electrons in the external circuit is from left to right and the chemical reaction goes spontaneously from right to left.

Unfortunately a number of different conventions have arisen for designating the setup of cells in connection with oxidation-reduction potentials and potentiometric titrations. For example, some writers express the Nernst equation for a single electrode potential at 25° as $E = E^0 + \frac{0.0591}{n} \log C$, while others use the form $E = E^0 - \frac{0.0591}{n} \log C$. The difference comes about in the derivation of the equation (see any text on physical chemistry). At one stage in the derivation we have $E = \frac{0.0591}{n} \log \frac{p}{p}$ where the two p's represent the solution tension of the electrode and the opposing osmotic pressure of the ions. If one substitutes these values in the equation so as to obtain $E = \frac{0.0591}{n} \log \frac{P}{C}$, where P is the solution tension and C is the concentration of the ions in solution, we have: $E = \frac{0.0591}{n} \log P - \frac{0.0591}{n} \log C$. The value of $\frac{0.0591}{n} \log P$ is a constant for a given metal at 25°, and assigning E^0 as this constant the equation becomes $E = E^0 - \frac{0.0591}{n} \log C$. But if one substitutes P and C in the inverse manner so as to obtain $E = \frac{0.0591}{n} \log \frac{C}{P}$, then the difference in potential between metal and solution becomes $E = \frac{0.0591}{n} \log C - \frac{0.0591}{n} \log P$. By assigning $-\frac{0.0591}{n} \log P$ as equal to E^0 the equation takes the form $E = E^0 + \frac{0.0591}{n} \log C$.

Furthermore, E^0 will be either positive or negative depending upon whether the reaction is considered as $Me^{n+} + ne \rightarrow Me^0$, or as $Me^0 \rightarrow Me^{n+} + ne$.

Again some writers give the e.m.f. of a cell as $E_1 - E_2$ while others prefer $E_1 + E_2$, the algebraic sum of the two single electrode potentials. But either form leads to the same result provided one is consistent in evaluating E_1 and E_2.

Still again, there are those who like to sketch the diagram of a cell in such a manner that the flow of electrons is always from right to left in the external circuit. There appears to be no intrinsic virtue in showing the flow of electrons always from right to left, or from left to right for that matter. The really important thing is that one always be able to reckon the direction of flow, whatever it be, so that the polarity of the cell is revealed.

Because of such variations in custom it is imperative that a set of conventions be chosen and thereafter consistently be followed. Any set of rules, if fundamentally sound, will lead to the same results and conclusions as any other set, provided only that once accepted they are consistently applied.

Electrode Potentials and Oxidation-Reduction Reactions

In the examples of single electrode potentials already mentioned a metal, or hydrogen, in a zero valence state was placed in contact with a solution of its ions. The reaction occurring

$$Me^{n+} + ne \rightleftarrows Me^0$$

was in each case an example of oxidation-reduction since there was an electron transfer, and in each case there was an electrode potential developed between metal and solution.

In the case of the hydrogen half-cell a noble metal like platinum constitutes the electrode, for at the surface of the platinum we have (adsorbed) hydrogen atoms surrounded by a solution of hydrogen ions. A difference in electrical potential also is set up if a noble metal dips into a solution containing ions which may exhibit two finite valences, e.g., Fe^{+++} and Fe^{++}. A cell may be arranged by combining such a half-cell with a hydrogen half-cell, that is,

$$Pt \left| \begin{matrix} Fe^{+++}\ (1\ M) \\ Fe^{++}\ \ (1\ M) \end{matrix} \right\| \begin{matrix} H^+\ (1\ M) \\ H_2\ (1\ atm.) \end{matrix} \Bigg| Pt$$

The e.m.f. of the above cell is found to be 0.78 volt. Therefore, since both half-cells are at standard state, $E^0_{Fe} = 0.78$.

Again we might set up the cell,

$$Pt \left| \begin{matrix} Ce^{++++}\ (1\ M) \\ Ce^{+++}\ \ (1\ M) \end{matrix} \right\| \begin{matrix} H^+(1\ M) \\ H_2\ (1\ atm.) \end{matrix} \Bigg| Pt$$

and we should find that the e.m.f. is 1.45 volts. Since both half-cells are at standard concentrations this is the value of E^0_{Ce}, i.e., 1.45.

If now we set up the cell,

$$Pt \left| \begin{matrix} Ce^{++++}\ (1\ M) \\ Ce^{+++}\ \ (1\ M) \end{matrix} \right\| \begin{matrix} Fe^{+++}\ (1\ M) \\ Fe^{++}\ \ (1\ M) \end{matrix} \Bigg| Pt$$

we have, since standard concentrations are specified, for the half-cell reactions

$$Ce^{++++} + e = Ce^{+++},\ E^0_{Ce} = 1.45$$
$$Fe^{+++} + e = Fe^{++},\ E^0_{Fe} = 0.78$$

and upon subtracting the latter from the former,

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++},\ E^0_{Ce} - E^0_{Fe} = 0.67$$

If these two solutions are connected by a salt bridge internally, a current of 0.67 volt will pass through the external circuit. The flow of electrons will be from right to left. This conforms with the fact that since the e.m.f. is positive the left-hand electrode is positive, that is, the cerium half-cell, and the electrons pass to the pole of higher positive charge. Also we note that since in this case the Ce^{++++}, Ce^{+++} system has the higher potential it is the oxidant, and the Fe^{+++}, Fe^{++} system is the reductant. Or we may simply say that, for the concentrations specified above, ferrous ion will be oxidized by ceric ion.

Electromotive Force and Concentration. If the cerium-iron cell described above is permitted to operate, the oxidation of ferrous ions and the simultaneous reduction of ceric ions will proceed, but not indefinitely. As the action continues the concentrations of all of the ions are changing, the ferric ion and cerous ion increasing while the ferrous ion and ceric ion are decreasing. Finally equilibrium conditions are established and at this point the e.m.f. of the cell, which has been decreasing as the cell operated, becomes zero. Obviously there must be a definite relation between e.m.f. and concentrations. There is, and the relation is obtained from the Nernst equation. For each of the two half-cells the Nernst equation states in general that

$$(1) \qquad E = E^0 + \frac{0.0591}{n} \log \frac{[\text{H.V.S.}]}{[\text{L.V.S.}]}$$

where [H.V.S.] and [L.V.S.] are concentrations of the ion in its higher valence state and its lower valence state respectively, and where n is the number of electrons involved when the ion passes from one valence state to the other.

The e.m.f. of the cell, of course, will be the difference between the two single electrode potentials, or $E_1 - E_2$, which, in general, yields

$$(2) \quad E_c = E_1 - E_2 = \left\{E^0_1 + \frac{0.0591}{n} \log \frac{[\text{H.V.S. (ion X)}]}{[\text{L.V.S. (ion X)}]}\right\} - \left\{E^0_2 + \frac{0.0591}{n} \log \frac{[\text{H.V.S. (ion Y)}]}{[\text{L.V.S. (ion Y)}]}\right\}$$

where we are thinking of the chemical reaction as being:

$$\text{X (high valence)} + \text{Y (low valence)} \rightarrow \text{X (low valence)} + \text{Y (high valence)}$$

If n has the same value for both ions, equation (2) becomes,

$$(3) \quad E_c = E_1 - E_2 = E^0_1 - E^0_2 - \frac{0.0591}{n} \log \frac{[\text{H.V.S. (ion Y)}][\text{L.V.S. (ion X)}]}{[\text{L.V.S. (ion Y)}][\text{H.V.S. (ion X)}]}$$

From the general formulations of equations (2) and (3) we may conclude:

1. If standard concentrations prevail for all concentrations within the brackets, or if the ratio of the numerator to the denominator is unity, then the e.m.f. of the cell is equal to $E^0_1 - E^0_2$, since $\log 1 = 0$.

2. None of the values within brackets may be zero, for then the logarithmic expression would become infinite. This means that there must always be a finite value for each of the several concentrations, though

under certain conditions some of them may be very small. In other words, oxidation-reduction reactions are reversible.

To illustrate the use of equation (3) suppose the concentrations in the cerium-iron cell are

$$[Ce^{++++}] = 10^{-5}$$
$$[Ce^{+++}] = 1$$
$$[Fe^{+++}] = 1$$
$$[Fe^{++}] = 10^{-5}$$

the reaction being written: $Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++}$. Substituting in equation (3),

$$E_c = 1.45 - 0.78 - 0.0591 \log \frac{(1)(1)}{(10^{-5})(10^{-5})}$$
$$= 0.67 - 0.0591 \log 10^{10}$$
$$E_c = 0.08 \text{ volt}$$

The e.m.f. of the cell is positive; according to the conventions we have adopted, this designates the polarity of the left electrode. Thus the cerium half-cell is the positive side and the chemical reaction spontaneously proceeds from left to right; that is, the iron is oxidized. Had the e.m.f. of the cell been negative, the Fe^{+++} would have oxidized the Ce^{+++}; this proves to be the case when the concentrations in the order given above for the four ions are 10^{-7}, 1, 1 and 10^{-7} respectively. The student should prove this by making the calculation.

The application of equation (2) for cases where n has different values for the two half-cells may be illustrated by the cerium-tin cell.

$$\text{Pt} \left| \begin{matrix} Ce^{++++} & (10^{-20}\ M) \\ Ce^{+++} & (10\ M) \end{matrix} \right\| \left. \begin{matrix} Sn^{++++} & (10\ M) \\ Sn^{++} & (10^{-20}\ M) \end{matrix} \right| \text{Pt}$$

As usual, we shall think of the chemical equation as though the left half-cell contains the ion acting as the oxidant, as is the case for standard concentrations. Whether it actually will be the oxidant or, instead, will be the reductant at the concentrations given, will be answered of course when we calculate the e.m.f. of the cell. We therefore write the chemical equation:

$$2Ce^{++++} + Sn^{++} \rightleftarrows 2Ce^{+++} + Sn^{++++}$$

Substituting in equation (2),

$$E_c = \left(1.45 + 0.0591 \log \frac{10^{-20}}{10}\right) - \left(0.15 + \frac{0.0591}{2} \log \frac{10}{10^{-20}}\right)$$
$$= 1.45 - 1.24 - 0.15 - 0.62$$
$$E_c = -0.56 \text{ volt}$$

Thus, since the e.m.f. is negative, the left-hand electrode is negative and the spontaneous chemical reaction taking place as the reaction proceeds

toward equilibrium is from right to left. That is to say, at these concentrations the Sn^{++++} ion oxidizes the Ce^{+++} ion, whereas at standard concentrations the reverse would be true.

Calculation of Equilibrium Constant. From equation (1) it is obvious that the single electrode potential for the cerium electrode is

$$E_1 = E^0_{Ce} + 0.0591 \log \frac{[Ce^{++++}]}{[Ce^{+++}]} \tag{4}$$

which also may be written

$$E_1 = E^0_{Ce} + \frac{0.0591}{2} \log \frac{[Ce^{++++}]^2}{[Ce^{+++}]^2}$$

and the single electrode potential for the tin electrode is

$$E_2 = E^0_{Sn} + \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

Now, solving for E_{cell},

$$E_c = E_1 - E_2 = E^0_{Ce} - E^0_{Sn} - \frac{0.0591}{2} \log \frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2}$$

The logarithmic expression, it will be noted, takes the form[5] of K_e for the reaction:

$$2Ce^{++++} + Sn^{++} \rightleftarrows 2Ce^{+++} + Sn^{++++}$$

In the preceding section it was shown that with the concentrations there employed the e.m.f. of this cell was negative; at standard concentrations for all four ions it is obvious that the e.m.f. of this cell will be $E^0_1 - E^0_2 = +1.30$ volts. Hence there must be concentrations somewhere in between these at which the e.m.f. would be zero. We may obtain the value of the equilibrium constant, therefore, if we set $E_c = 0$, and solve for the value of the logarithmic term thus:

$$0 = E^0_{Ce} - E^0_{Sn} - \frac{0.0591}{2} \log \frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2}$$

$$0 = 1.45 - 0.15 - \frac{0.0591}{2} \log \frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2}$$

$$\frac{0.0591}{2} \log \frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2} = 1.30$$

$$\log \frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2} = \frac{1.30}{0.0591/2} = 43.9$$

or

$$\frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2} = 8 \times 10^{43} = K_e, \text{ at } 25°$$

[5] Note that the logarithmic expression resembles the equilibrium constant. Actually it equals K_e only when the cell reaction is at equilibrium, i.e., when the actual concentrations are the equilibrium concentrations.

This large value means of course that the equilibrium point for the oxidation of Sn^{++} by Ce^{++++} lies far to the right, that is, the oxidation is practically complete.

Approach Toward Completeness of Reaction. Having evaluated the equilibrium constant for a given reaction, it is possible to calculate how nearly complete the reaction is when equilibrium has been attained.

Suppose that Sn^{++} is titrated with Ce^{++++} solution and that the tin solution originally contained 5 millimoles of Sn^{++} and that the volume, at the stoichiometric point, is 250 ml.

First it is necessary to evaluate the four ionic concentrations as follows:

Let $[Sn^{++}] = X$ at the stoichiometric point.

$[Sn^{++++}] = \frac{5}{250} = 2 \times 10^{-2}$ millimoles/ml. = moles/l., for practically all of the tin is oxidized at the stoichiometric point.

$[Ce^{+++}] = 4 \times 10^{-2}$, since the concentration of the Ce^{+++} formed must be twice that of Sn^{++++}.

$[Ce^{++++}] = 2X$, since when chemically equivalent quantities have been brought together there are, for each unoxidized Sn^{++} ion, two unreduced Ce^{++++} ions.

Substituting the above concentrations in the equilibrium expression, namely,

$$\frac{[Sn^{++++}][Ce^{+++}]^2}{[Sn^{++}][Ce^{++++}]^2} = 8 \times 10^{43}$$

we obtain

$$\frac{(2 \times 10^{-2})(4 \times 10^{-2})^2}{(X)(2X)^2} = 8 \times 10^{43}$$

Solving for X,

$$4X^3 = \frac{(2 \times 10^{-2})(4 \times 10^{-2})^2}{8 \times 10^{43}}$$

$$X = 5 \times 10^{-17} \text{ moles per l. } (= 1 \times 10^{-15} \text{ mg. } Sn^{++} \text{ in 250 ml.})$$

This is the amount of tin which escapes oxidation at the stoichiometric point. Evidently, for all practical purposes, the reaction may be considered complete.

Change of Oxidation Potential During Titration

We may follow the change in potential established by the indicator electrode immersed in the titrating solution—for example, in the titration of stannous tin by ceric cerium—by calculating several values of the potential during the titration. Let it be emphasized that what we are now computing is not the e.m.f. of the cell which functions during the titration. The e.m.f. of the complete cell is $E_1 - E_2$ and at a given point in

the titration the e.m.f. will have different values if a calomel electrode, the quinhydrone electrode or the hydrogen electrode, etc., completes the system of which the cerium-tin, platinum electrode is the other part. On the contrary, we are now about to calculate the changing potential of the cerium-tin, platinum electrode itself. The potential established after the addition of various amounts of oxidizing solution from the buret is a function (up to the stoichiometric point) of the stannic-stannous ratio. For example, in titrating 100 ml. of 0.1 *N* stannous tin with a 0.1 *N* solution of ceric ion the potential after the addition of 9.09 ml. of the oxidant is calculated as follows.

$$E = E^0_{Sn} + \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

$$E = 0.15 + \frac{0.0591}{2} \log \frac{9.09}{90.91}$$

(Note that the ratio of the milliliters is the same as the ratio of the concentrations since the volume is constant.)

$$E = 0.15 + \frac{0.0591}{2} \log 0.10$$

$$E = 0.15 - 0.03 = 0.12 \text{ volt}$$

After the addition of 90.91 ml. of ceric solution we have

$$E = 0.15 + \frac{0.0591}{2} \log \frac{90.91}{9.09}$$

$$E = 0.15 + 0.03 = 0.18 \text{ volt}$$

After 99 ml. of ceric solution

$$E = 0.15 + \frac{0.0591}{2} \log \frac{99}{1}$$

$$E = 0.15 + 0.06 = 0.21 \text{ volt}$$

After 99.9 ml. of ceric solution

$$E = 0.15 + \frac{0.0591}{2} \log \frac{99.9}{0.1}$$

$$E = 0.15 + 0.09 = 0.24 \text{ volt}$$

Before calculating the potential at the stoichiometric point note that the chemical equation for the titration reaction is

$$2Ce^{++++} + Sn^{++} \rightleftarrows 2Ce^{+++} + Sn^{++++}$$

Thus at the stoichiometric point

$$\frac{[Ce^{++++}]}{2} = [Sn^{++}]$$

and

$$\frac{[Ce^{+++}]}{2} = [Sn^{++++}]$$

or

$$\frac{[Ce^{++++}]}{2} \Big/ \frac{[Ce^{+++}]}{2} = \frac{[Sn^{++}]}{[Sn^{++++}]} \text{ so that}$$

$$\frac{[Ce^{++++}]}{[Ce^{+++}]} = \frac{[Sn^{++}]}{[Sn^{++++}]} \tag{5}$$

Now at the stoichiometric point $E_{Ce} = E_{Sn} = E_{Stoich.\ pt.}$
From equation (1) we have

$$E_{Ce} = E^0_{Ce} + 0.0591 \log \frac{[Ce^{++++}]}{[Ce^{+++}]} \tag{6}$$

Similarly,

$$E_{Sn} = E^0_{Sn} + \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} \tag{7}$$

By doubling equation (7) and adding equation (6) we obtain[6]

$$3E_{Stoich\ pt} = E^0_{Ce} + 2E^0_{Sn} + 0.0591 \log \frac{[Ce^{++++}][Sn^{++++}]}{[Ce^{+++}][Sn^{++}]} \tag{8}$$

Since from equation (5)

$$\frac{[Ce^{++++}]}{[Ce^{+++}]} = 1 \Big/ \frac{[Sn^{++++}]}{[Sn^{++}]}$$

it follows that the logarithmic term of equation (8) is equal to unity and the logarithm of that term is zero. Accordingly, equation (8) becomes

$$3E_{Stoich.\ pt.} = E^0_{Ce} + 2E^0_{Sn}$$

or

$$E_{Stoich.\ pt.} = \frac{1.45 + 0.30}{3} = 0.57 \text{ volt} \tag{9}$$

For points past the stoichiometric point the potential is calculated from the ratio of $[Ce^{++++}]$ to $[Ce^{+++}]$ combined with E^0_{Ce}, 1.45 volts. Thus after 100.1 ml. of ceric solution

[6] For reactions in which only one ion of each reactant is involved the electrode potential at the stoichiometric point is, of course, half of the sum (i.e., the mean) of the two E^0 values. For details of the situation when ferrous iron ion is titrated with ceric ion, see Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, 1943, p. 487.

In general for a reaction: $aOx_1 + bRed_2 \rightleftarrows aRed_1 + bOx_2$ the potential at the stoichiometric point is:

$$E_{Stoich.\ pt.} = \frac{bE^0_1 + aE^0_2}{a + b}$$

$$E = E^0_{Ce} + 0.0591 \log \frac{[Ce^{++++}]}{[Ce^{+++}]}$$

$$E = 1.45 + 0.0591 \log \frac{0.1}{100} = 1.27 \text{ volts}$$

In a like manner the potential may be calculated for additions of 101 ml., 110 ml. and 120 ml. of ceric solution with resulting values of 1.33, 1.39 and 1.41 volts respectively. These data are plotted in Fig. 29.

The potential increases sharply in the neighborhood of the stoichiometric point. As a result the stoichiometric point may be ascertained in potentiometric titrations by plotting the potential (usually the e.m.f. of

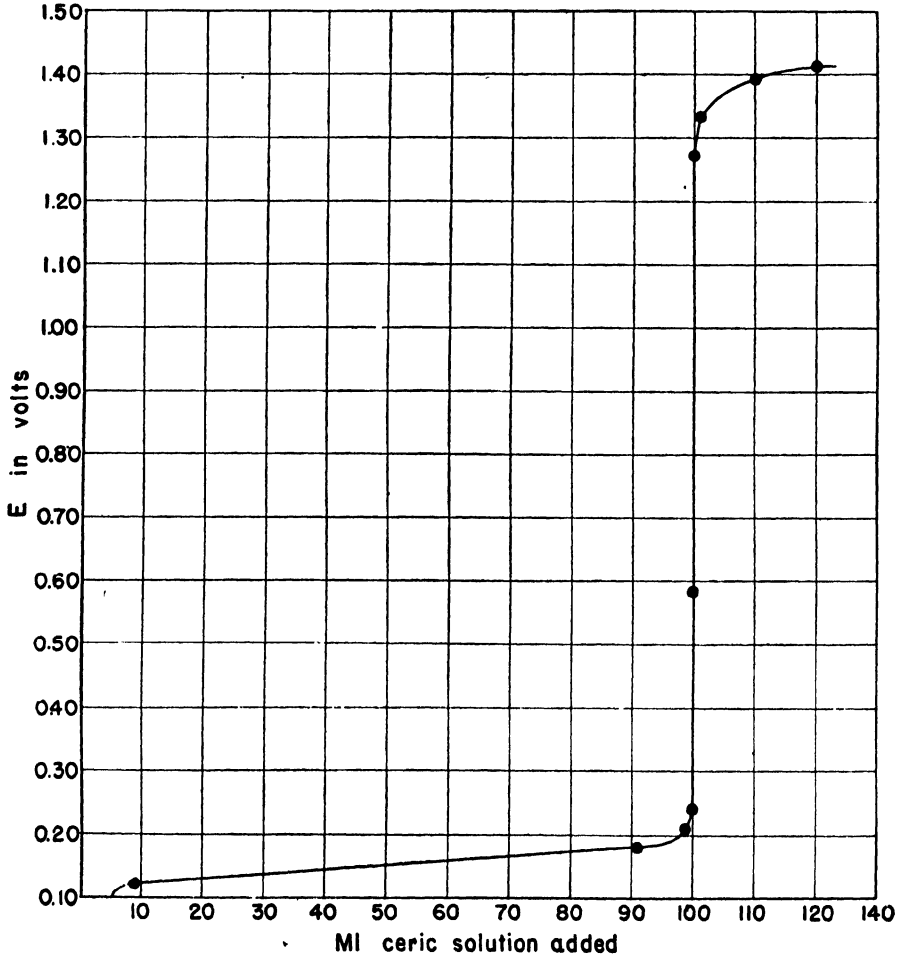


FIG. 29. Change in potential in titration of 100 ml. of 0.1 *N* stannous tin with 0.1 *N* ceric solution at 25°.

the cell; see below) against milliliters of solution added from the buret and dropping a perpendicular from the steepest point on the curve. The number of milliliters so obtained on the abscissa gives the end point of the titration. Done in this manner no color indicator is needed.

Let it be repeated here that the values in volts plotted in Fig. 29 represent the single electrode potential between the platinum electrode and the titrated solution. The cell e.m.f. read on the potentiometer will depend not only upon these values but, in addition, upon what constitutes the other electrode. If the molar hydrogen electrode comprises the other half-cell then the numerical values given above for the ceric-stannous titration would remain as they stand since the molar hydrogen electrode has a potential of zero. If, however, the calomel electrode were used in the ceric-stannous titration the e.m.f. would differ from those given above to an extent governed by the potential of the calomel electrode itself. For example, with the normal calomel electrode the cell for this titration is represented

$$\begin{matrix} Hg \\ Hg_2Cl_2 \end{matrix} \Big| \; KCl\ (1\ M) \; \Big\| \begin{matrix} Sn^{++++} \\ Sn^{++} \end{matrix} \Big| \; Pt$$

(The calomel half-cell is placed on the left since it has a higher positive potential than the tin half-cell at standard concentrations.) The e.m.f. developed is calculated from

$$E_c = E_1 - E_2 = E^0_{Calomel} - \left(E^0_{Sn} + \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} \right)$$

$$= 0.28 - 0.15 - \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

For example, after 90.91 ml. of ceric solution has been added,

$$E_c = 0.13 - \frac{0.0591}{2} \log \frac{90.91}{9.09}$$

$$E_c = 0.13 - 0.03 = 0.10 \text{ volt}$$

In a similar manner the e.m.f. to be expected on the potentiometer may be calculated for all additions of ceric solution throughout the titration.

Oxidation-Reduction Indicators

The Oxidizing or the Reducing Agent May Serve as Its Own Indicator. If the reagent used in an oxidation-reduction titration is highly colored and if it is converted as it undergoes reaction into a colorless compound, the end point is revealed by the appearance of color when one excess drop of reagent has been added. Potassium permanganate is one of the most valuable oxidizing agents in quantitative work because of this property. Added to a reducing solution it is converted into colorless manganous compounds until there is practically no reductant left; then one excess drop of permanganate gives a pink tint even in a total volume of several hundred milliliters.

Solutions of iodine when dilute have a yellow color. Titrations with iodine or those producing iodine show the stoichiometric point by the disappearance or the appearance of the yellow tint. As a rule, however, starch is added to such solutions shortly before the end point because starch is a specific indicator for iodine, yielding the familiar intensely blue color. Ceric ions also have a yellow color, and with some practice one may detect the end point of titrations involving this oxidant without the use of a specific indicator.

Internal Oxidation-Reduction Indicators. It will be remembered that indicators for acid-base titrations are weak organic acids or bases which exhibit the property of changing color when the pH of the solution in which they are used is varied over a small pH range. It also will be recalled that the proper indicator for acidimetry is one which undergoes the color change at a pH close to that which the titrated solution will have at the stoichimetric point.

An oxidation-reduction indicator presents a similar problem except that we are directly concerned with the potential characterizing the indicator. An oxidation-reduction indicator is a substance which has different colors in the oxidized and in the reduced states, and which may undergo oxidation and reduction reversibly. Just as is the case with any oxidant, there is an oxidizing potential associated with every oxidation-reduction indicator, and the proper indicator for a given titration is one the potential of which coincides with that established at the stoichiometric point by the system present in the titration.

Assume, for example, that an unknown ferrous iron solution is being titrated by a ceric solution of known normality. At the stoichiometric point the potential of the system will be

$$E_{\text{Stoich. pt.}} = \frac{E^0_{Ce} + E^0_{Fe}}{2} = \frac{1.45 + 0.78}{2} = 1.12 \text{ volts}$$

Thus for this titration, with ceric solution used as the oxidizing agent, the indicator should have a potential of around 1.1 volts. Accordingly *orthophenanthroline-ferrous* ion, commonly called "Ferroin," shown in Table 17 to have a potential of 1.14 volts, would be suitable and is in fact much used for this titration. It changes in color from red to pale blue when oxidized.

COMMONLY USED OXIDATION-REDUCTION INDICATORS. A considerable number of these indicators have come into use ranging in potential from around 0.25 volt to about 1.3 volts.[7] In addition to "Ferroin," just mentioned, the following are typical of those most widely used.

[7] See Kolthoff and Stenger, *Volumetric Analysis*, Vol. I, Interscience Publishers, New York, 1942, p. 140; and Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, 1943, p. 496.

Diphenylamine and diphenylbenzidine are only slightly soluble in water but they do dissolve in sulfuric acid. Made up in solutions containing 1 g. per 100 ml. of concentrated sulfuric acid they may be employed a few drops to a titrated solution of 200 to 300 ml. At an oxidation potential above 0.76 volt the color is violet; below 0.76 volt, colorless.

Diphenylamine Sulfonic Acid. The sodium salt is usually used. The color change occurs at a potential of 0.84 volt. In the reduced form it is green, whereas the oxidized form is reddish violet. It is prepared as 0.2 to 0.5 per cent solutions of the salt in water. It may be used in the titration of ferrous iron; after the end point is reached the color changes slowly on standing. While neither diphenylamine nor diphenylbenzidine can be used as indicators in the presence of tungstates, since they form insoluble tungstates, diphenylamine sulfonic acid can be used in such a solution. This is an important advantage since iron ores often contain tungsten compounds. Another advantage of this indicator is that the color is so pronounced that the change may be observed when dichromate is the oxidant in spite of the green chromic ion color which that oxidant produces when it is reduced.

Similar to "Ferroin," as far as color change is concerned, is the ferrous ion complex of *nitro-orthophenanthroline.* This indicator is known as "Nitro-Ferroin" and has a high oxidation potential of 1.25 volts.

Problems

1. (a) Calculate the e.m.f. of the cell

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Ce^{++++}}\ (10^{-7}\ M)\\ \mathrm{Ce^{+++}}\ \ (1\ M)\end{matrix}\right\|\left.\begin{matrix}\mathrm{Fe^{+++}}\ (1\ M)\\ \mathrm{Fe^{++}}\ \ (10^{-7}\ M)\end{matrix}\right|\mathrm{Pt}$$

(b) Which electrode is positive? (c) In what direction will the chemical reaction proceed?

Answer: (a) $E_{cell} = 0.16$ volt; (b) positive electrode is Fe^{+++}, Fe^{++}; (c) reaction goes spontaneously from right to left, i.e., Fe^{+++} oxidizes Ce^{+++}.

2. (a) Calculate the e.m.f. of the cell

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Fe^{+++}}\ (0.1\ M)\\ \mathrm{Fe^{++}}\ \ (0.01\ M)\end{matrix}\right\|\left.\begin{matrix}\mathrm{Sn^{++++}}\ (0.01\ M)\\ \mathrm{Sn^{++}}\ \ (0.1\ M)\end{matrix}\right|\mathrm{Pt}$$

(b) Which electrode is positive? (c) In what direction will the chemical reaction proceed?

Answer: (a) $E_{cell} = 0.72$ volt; (b) positive electrode is Fe^{+++}, Fe^{++}; (c) reaction proceeds spontaneously from left to right, i.e., Fe^{+++} oxidizes Sn^{++}.

3. From the general equation for the single electrode potentials for the ceric-cerous system and for the ferric-ferrous system, and from the values of E^0_{Ce} and E^0_{Fe} taken from Table 17, calculate the equilibrium constant for the reaction:

$$\mathrm{Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++}}$$

Answer: 2.2×10^{11}.

4. (a) Calculate the equilibrium constant for the reaction:

$$MnO_4^- + 8H^+ + 5Fe^{++} \rightleftarrows 5Fe^{+++} + Mn^{++} + 4H_2O$$

(b) A solution containing 5 millimoles of Fe^{++} is titrated with 0.5000 *N* $KMnO_4$ solution. If the final volume is 250 ml. what weight of iron remains unoxidized at the end point if 0.03 ml. excess $KMnO_4$ solution is added and the hydrogen ion concentration is 1 *M*? (Remember that the equation for the electrode potential of the ferric-ferrous system must be multiplied by 5 in order to balance the over-all chemical equation, but that E^0_{Fe} nevertheless remains 0.78. Note too that the mole fraction of water is practically unity so that we may substitute 1 as the activity for water.)

Answer: (a) 8.5×10^{60}; (b) 5.8×10^{-13} g. of Fe^{++} in 250 ml.

5. From the oxidation-reduction potentials from Table 17 for $H_2O + e = \frac{1}{2}H_2 + OH^-$, $E^0 = -0.83$ and for $H^+ + e = \frac{1}{2}H_2$, $E^0 = 0.00$, show that the ion product of water at 25°, K_w, has a value of approximately 10^{-14}. (Remember the activity of water $\cong$ 1.)

6. What is the electrode potential at the stoichiometric point when a solution of ferrous iron is titrated with a solution of ceric ion?

Answer: 1.12 volts.

Chapter 11

OXIDATION AND REDUCTION III. EXPERIMENTAL

Potassium Permanganate Processes

Potassium permanganate solution is probably the most widely used oxidant in quantitative analysis. This is largely due to three advantages. First, potassium permanganate has a high oxidation potential (see Table 17) and therefore oxidizes a great many reductants. Second, the reactions between permanganate ion and the majority of reducing substances proceed rapidly. Third, due to the fact that permanganate solution is deeply colored, this oxidant acts as its own indicator, one excess drop of the 0.1 *N* solution imparting a distinct color even to 300 ml. of solution. On the other hand, this reagent has some disadvantages. It cannot be obtained in a perfectly pure state, even the highest grade containing some manganese dioxide. A standard solution cannot be prepared, therefore, by accurately weighing out a definite quantity and dissolving in an exact volume of solution. Instead, a solution of approximately the desired concentration is prepared, after which it must be standardized against a suitable standard. Before standardizing the solution it must be allowed to react with the small amount of organic matter present in the distilled water. This results in the formation of manganese dioxide,

$$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O$$

and manganese dioxide catalyzes the reaction,

$$4MnO_4^- + 2H_2O \rightarrow 4OH^- + 4MnO_2 + 3O_2$$

Obviously then, in order to obtain a stable permanganate solution for standardization, it must be freed from organic matter and from manganese dioxide. Another limitation is that hydrochloric acid cannot be used to acidify solutions which permanganate is to oxidize since the chloride ion is oxidized to chlorine by permanganate.[1] As a rule sulfuric acid is used instead. In cases where hydrochloric acid has been employed to bring a sample into solution, the solution must be evaporated with sulfuric acid in order to expel the hydrochloric before titrating with permanganate.

[1] Baxter and Zanetti, *Am. Chem. J.*, **33**, 500 (1905).

In acid solution permanganate takes up five electrons when it functions as an oxidant,

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$$

whereas in neutral or basic solution three electrons are involved.

$$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$$

Potassium permanganate solution is used in many quantitative determinations. Among the most common are those involving the following oxidations occurring in acid solution:

$$Fe^{++} - e = Fe^{+++}$$
$$As^{+++} - 2e = As^{+++++}$$
$$Sb^{+++} - 2e = Sb^{+++++}$$
$$Sn^{++} - 2e = Sn^{++++}$$
$$V^{++} - 2e = V^{++++}$$
$$Ti^{+++} - e = Ti^{++++}$$
$$U^{++++} - e = U^{+++++}$$
$$Mo^{+++} - 3e = Mo^{++++++}$$
$$C_2O_4^{=} - 2e = 2CO_2$$
$$H_2O_2 - 2e = O_2 + 2H^+$$
$$H_2S - 2e = S + 2H^+$$

Preparation of 0.1 *N* Solution of Potassium Permanganate. The equivalent weight of potassium permanganate, used in acid solution, is 158.03/5 = 31.61. For a liter of 0.1 *N* solution, therefore, weigh out roughly 3.2 g. of the solid. Dissolve in approximately 1 l. of distilled water and heat the solution in a large beaker until it boils. Then place over a steam bath for 2 hours, after which let the solution stand overnight or longer. This will allow time for oxidation of reducing agents in the water.

Filter the solution through an asbestos mat into a glass-stoppered bottle. The solution should be kept in the dark, or if preferred the storage bottle may be covered entirely with a black cloth wrapper and equipped with a siphon. In the latter case use a two-hole stopper and insert a calcium chloride tube containing a desiccant.

Notes. The solution is filtered to remove MnO_2 which was present in the original crystals and which was formed as a result of reduction by organic matter.

An asbestos filter must be used instead of filter paper since fibers from the latter would introduce more organic matter into the solution.

If a siphon is attached to the storage bottle it should be equipped with a glass stopcock. No rubber tube connections should be used. A calcium chloride tube plugged with cotton and then filled with a desiccant serves as the air inlet to the bottle.

Standardization. Sodium oxalate serves as the most satisfactory primary standard for permanganate solutions. It meets all of the criteria for standards in general. Although the reaction between permanganate ion and oxalate ion is not so simple as indicated in the following equation,

$$2MnO_4^- + 5C_2O_4^= + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O$$

the equation does indicate the stoichiometric relationship involved. Many studies have been made of the reaction.[2]

Procedure. Dry some pure sodium oxalate for 2 hours at 110°, cool and place in a glass-stoppered bottle which is kept in a desiccator. Weigh samples of about 0.2 g., transfer to 400 ml. beakers and dissolve in 200 ml. of 5:95 sulfuric acid. Stir until all of the oxalate has dissolved. Calculate roughly the volume of permanganate expected for the titration and rapidly add about 90 per cent of this volume from the buret. Allow to stand until the solution has lost its color. Heat the solution to 55° to 60° and complete the titration by adding the permanganate slowly, being careful that the color has disappeared entirely before adding the next drop. The end point has been reached when a definite pink hue which lasts for 30 seconds is obtained. Run a blank in order to see whether or not the diluent effect would cause an error; that is, see if 1 drop of the permanganate solution will color for 30 seconds 250 ml. of 5:95 sulfuric acid. If a zero blank is not obtained, make the appropriate correction. From the weight of the sodium oxalate and the volume of permanganate used calculate the exact normality of the solution. The relative mean deviation should not exceed 1 part per 1000 for duplicate results.

Notes. The reaction between permanganate and oxalate is catalyzed by the manganous ion. Thus the permanganate color fades slowly after the initial addition but after further additions the color fades rapidly because the reaction produces its own catalyst. In other words, the reaction is autocatalytic.

Between 55° and 60° the reaction proceeds rapidly. Above 60° there is some danger of decomposition of oxalic acid which has been formed from the combination of hydrogen and oxalate ions: $H_2C_2O_4 \rightarrow H_2O + CO_2 + CO$.

OTHER PRIMARY STANDARDS FOR PERMANGANATE

Arsenious Oxide. Arsenious oxide can be obtained as pure as 99.97 per cent As_2O_3. It serves as an excellent standard for permanganate with which it reacts rapidly and quantitatively when catalyzed with a trace of iodide ion. Chloride ion does not interfere.

Procedure. Accurately weigh out portions of about 0.2 g. of pure arsenious oxide and transfer to 250 ml. beakers. Dissolve in 10 ml. of 3 *N* sodium hydroxide which is free from oxidizing or reducing agents

[2] Fowler and Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935); McBride, *J. Am. Chem. Soc.*, **34**, 393 (1912); Launer and Yost, *ibid.*, **56**, 2571 (1934).

and add 75 ml. of 1:10 hydrochloric acid. Add a drop of 0.002 *M* potassium iodide as a catalyst. Titrate with the permanganate solution until finally 1 drop causes a pink color which persists for 30 seconds or longer. The end point may be secured, if preferred, by using a drop of 0.02 *M* orthophenanthroline-ferrous compound as an indicator. The relative mean deviation should not exceed 1 part per 1000.

Iron Wire. Pure iron may serve as a primary standard for permanganate solutions, but care must be taken to obtain a pure sample and to see that it is bright and clean, that is, free from traces of rust.

Procedure. Clean with fine emery paper a length of pure iron wire which will weigh about 0.25 g., then wipe first with a piece of moist Kleenex and then with a dry piece. Weigh the wire accurately. The iron must be brought into solution and converted completely into the ferrous state before titrating. Depending upon whether the reduction is to be accomplished with the Jones reductor or by the Zimmermann-Reinhardt method, the wire is dissolved either in sulfuric acid or in hydrochloric acid. If the Jones reductor method is to be used dissolve the iron by heating gently with 10 ml. of 1 *M* sulfuric acid, after which proceed with the reduction and titration as described under the procedure on p. 194 beginning with the sentence: "Cool the solution and dilute carefully to 100 ml. . . . " (Of course no filtration will be necessary here.) If the Zimmermann-Reinhardt method is preferred dissolve the wire by gentle warming in 30 ml. of 6 *N* hydrochloric acid and proceed with the reduction and titration as described under the procedure on p. 191 beginning with: "To the hot solution add dropwise a freshly prepared solution of stannous chloride . . . "

Determination of Iron in an Ore. Permanganate Method

The most abundant iron ores are limonite, $Fe_2O_3.xH_2O$; hematite, Fe_2O_3; and magnetite, Fe_3O_4. These ores contain varying quantities of silica and small amounts of other substances including, sometimes, organic matter. Three steps are involved in the determination of iron with permanganate: the solution of the iron in the ore; the conversion of all the iron to the ferrous state and the prevention of interference of other reducing ions; and the titration of the ferrous ions with the standard permanganate solution.

The sample should be finely ground and if organic matter is present it should be roasted at a dull red heat in a porcelain crucible for 10 minutes. Iron ores usually do not dissolve in sulfuric or nitric acids, but as a rule are easily brought into solution with hydrochloric acid, especially if a little stannous chloride is added. A residue of silica remains and if it is colored the solution should be filtered and the residue fused with sodium carbonate. The fusion then is treated with acid to bring its iron into solu-

tion and this solution is added to the original. Ores not responding to the sodium carbonate fusion should be treated with potassium bisulfate (see p. 7).

Reduction of Ferric Ion. The reduction of ferric iron in the solution prior to titration with permanganate may be accomplished by four different methods: reduction with hydrogen sulfide, with sulfur dioxide, with stannous chloride or with a metal like zinc. It is always necessary to remove any excess of reducing agent since otherwise the permanganate would react with these reductants in addition to reacting with the ferrous iron. The removal of the excess reducing agent is effected in the first two cases by boiling the solution in an atmosphere of carbon dioxide. Excess stannous chloride is destroyed by oxidation with mercuric chloride. If zinc is used as the reductant no excess reducing agent is introduced into the iron solution. The two last methods for reduction will be taken up in detail.

ZIMMERMANN-REINHARDT REDUCTION. The ore is dissolved in a hydrochloric acid solution. In the presence of ferric iron the chloride ion is oxidized by permanganate unless a "preventive solution"[3] containing manganous ions is used to lower the oxidation potential of permanganate to a value below that necessary for the oxidation of chloride. The preventive solution also lowers the oxidation potential of ferrous ion, by formation of the complex, $Fe(PO_4)_2^{\equiv}$, so that the permanganate still will react quantitatively with the iron.[4]

Procedure. Accurately weigh samples of about 0.5 g. of the finely divided, dry ore. If organic matter is suspected place the samples in porcelain crucibles and heat to a dull red heat for 10 minutes; then cool and place the crucibles in 100 ml. beakers. Next treat with acid as described below and remove the crucibles by lifting with a stirring rod and rinsing completely with a stream of water from a wash bottle. If no organic matter is present the roasting may be omitted and the samples treated with acid after weighing and directly transferring to 600 ml. beakers.

Add 30 ml. of 6 *N* hydrochloric acid, cover the beaker with a watch glass and heat to just below the boiling point for 30 minutes or longer, until the silica residue is white or gray. (If the residue is still colored after heating for an hour consult the instructor about fusing.) To the hot solution add dropwise a freshly prepared solution of stannous chloride, made by dissolving 15 g. of $SnCl_2.2H_2O$ in 100 ml. of 1:2 hydrochloric

[3] Preparation of "preventive solution": Dissolve 70 g. of $MnSO_4.4H_2O$ in 500 ml. of water. Add 125 ml. of concentrated H_2SO_4 and 125 ml. of 85 per cent H_3PO_4. Dilute to 1000 ml.

[4] See also "Theory of Preventive Solution," Fales and Kenny, *Inorganic Quantitative Analysis*, D. Appleton-Century Co., New York, 1939, p. 423.

acid. The yellowish color of the ferric ion should now disappear. Add a drop or two of stannous chloride in excess, but no more. Cool the solution and pour in quickly 10 ml. of saturated mercuric chloride solution. Allow to stand for 3 minutes. A white, silky precipitate should result. (Should no precipitate appear too little stannous chloride was added, while the formation of a black or gray precipitate indicates that too large an excess of stannous chloride was present and the analysis must be started again from the beginning.) Transfer quantitatively to a 600 ml. beaker or Erlenmeyer flask, add about 350 ml. of water and 25 ml. of preventive solution. Titrate at once with standard permanganate solution. The end point has been reached when 1 drop imparts a faint pink color which persists for 15 seconds or longer.

A blank must be run since a small but significant volume of permanganate must be added after the stoichiometric point is reached to render the color visible in such a large volume of solution. Add 2 drops of stannous chloride to 30 ml. of 6 *N* hydrochloric acid and proceed with all of the steps of the determination. Subtract the small volume of permanganate required by the blank from that necessary for the analysis. Calculate the percentage of iron in the ore. The relative deviation from the mean should not exceed 3 parts per 1000.

Notes. The stannous chloride reduces the ferric ion: $2Fe^{+++} + Sn^{++} + 6Cl^- \rightarrow 2Fe^{++} + SnCl_6^-$. The excess stannous ion is then removed by adding mercuric ion: $Sn^{++} + 2HgCl_2 + 4Cl^- \rightarrow SnCl_6^- + Hg_2Cl_2\downarrow$. The mercurous chloride remaining in the solution does no harm since it is insoluble and reacts with permanganate inappreciably in cold solutions.

Too large an excess of stannous chloride may cause the reduction of mercurous chloride, first formed, to metallic mercury: $Sn^{++} + Hg_2Cl_2 + 4Cl^- \rightarrow SnCl_6^- + 2Hg\downarrow$. This renders the analysis worthless since mercury slowly reduces the permanganate during the titration.

The solution should be cooled to room temperature after reduction with stannous chloride, for oxygen in the air would oxidize much of the ferrous ions if the solution remained hot.

REDUCTION BY THE JONES REDUCTOR. If the sample can be dissolved in sulfuric acid, so much the better; if hydrochloric acid must be used to bring the sample into solution and if permanganate is to be the oxidant used in the titration, then the solution is fumed with sulfuric acid to expel HCl. Following the fuming the solution is diluted and passed through the Jones reductor which converts the ferric ions to the ferrous state. The solution then may be titrated without the use of preventive solution since no chloride ion is present. Only vanadium and molybdenum interfere with iron determination by the Zimmermann-Reinhardt method, but, in addition, titanium and chromium introduce error when the Jones reductor method is used.

THE REDUCTOR. Zinc is the metal most commonly used for the reduction of ferric ions, though cadmium and aluminum are often used. Zinc may be obtained free from iron but it should be tested for purity. Amalgamated zinc is preferred to the metal alone since the amalgamation prevents the liberation of hydrogen because of the high overvoltage of hydrogen on mercury (see p. 305).

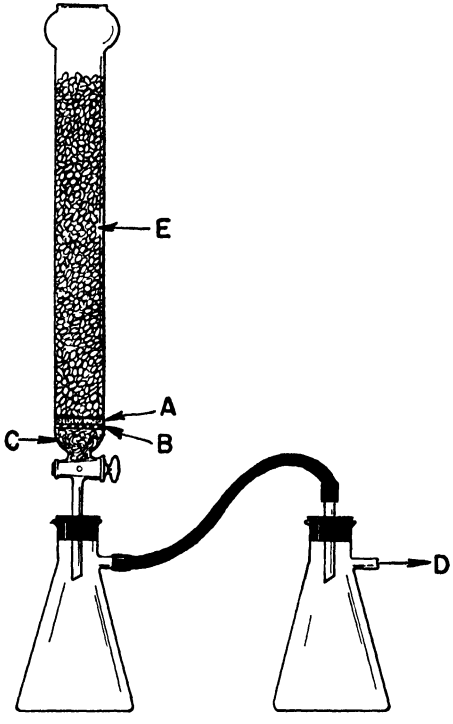


FIG. 30. The Jones reductor. (*A*) Asbestos mat. (*B*) Perforated disk. (*C*) Wad of glass wool. (*D*) To suction. (*E*) Zinc amalgam.

The Jones reductor[5] consists of a glass tube about 2 cm. in diameter and some 25 to 30 cm. in length. It is enlarged or flared at one end and is equipped with a stopcock at the lower end, as seen in Fig. 30. A perforated porcelain disk, such as is used in Gooch crucibles, is placed in the reductor above a wad of glass wool, and a mat of asbestos is seated on the disk. The amalgamated zinc is lightly packed over the supporting disk until it fills the reductor to within 2 or 3 cm. of the top. The reductor is connected to a suction flask as shown in the figure. The amalgamated zinc may be prepared as follows: Treat 300 g. of 20–30 mesh, pure granu-

[5] See Stone and Hume, *Ind. Eng. Chem., Anal. Ed.*, **11**, 598 (1939).

lated zinc with 300 ml. of 2 per cent mercuric chloride solution acidified with 2 ml. of concentrated nitric acid. Stir for 5 minutes, decant and wash several times with water. The zinc should now be covered with a layer of mercury and possess a bright luster. When the reductor has been filled with the amalgam, wash several times with water and then pass through 100 to 200 ml. of 1 *N* sulfuric acid, never allowing (from this point on) the top of the amalgam to be exposed to air; that is, keep the level of the liquid in the reductor above the amalgam. Test a 200 ml. portion of 1 *N* sulfuric acid, after it has been through the reductor, by adding 1 drop of 0.1 *N* permanganate solution. If the permanganate does not impart a pink color the reductor must be washed further with acid until a 200 ml. portion is colored with 1 drop of permanganate. The reductor then is said to have a zero blank value.

Silver as a Reductor.[6] The silver reductor is similar to the Jones reductor except that metallic silver acts as the reductant instead of amalgamated zinc. This reductor has been employed for the determination of iron by ceric sulfate. The silver reductor has certain advantages over the Jones reductor. In the first place it shows a zero blank day after day for months. Furthermore, it does not reduce titanium which, therefore, is not an interfering metal in the analysis of ores if they are reduced with silver. In addition, low concentrations of nitric acid and of ammonium ion present no complications.

The silver reductor may be set up in a manner similar to the preparation of the Jones reductor. A reductor tube 2 cm. in diameter and 10 to 15 cm. in length suffices. To prepare the silver dissolve 30 g. of silver nitrate in 500 ml. of water and acidify with 5 drops of nitric acid. Then immerse a strip of pure sheet copper having about 100 sq. cm. surface area. The silver will be thrown out of solution. Stir occasionally. Finally when practically all of the silver has been precipitated, wash the spongy mass with 1:20 sulfuric acid, place the metal in the tube and wash again with 200 ml. of *N* hydrochloric acid. Though exposure to air causes no finite blank, the column of silver should be kept covered with liquid. After repeated use the reductor accumulates silver chloride but it is quickly regenerated by filling with 1:20 sulfuric acid and dipping a rod of zinc into the mass of silver. The silver chloride is soon reconverted to metallic silver.

Procedure. Accurately weigh samples of iron ore of about 0.5 g. and treat exactly as described on p. 191, up to the point where stannous chloride was added. Do not add stannous chloride. To the resulting ferric chloride solution add carefully 5 ml. of 18 *M* sulfuric acid and evaporate, without boiling, until all the hydrochloric acid has been volatilized; that is, until sulfuric acid fumes are noted. Cool the solution and dilute carefully to 100 ml. with water, then filter and wash the paper and residue five times with 1:20 sulfuric acid. Run the solution through the Jones reductor under gentle suction at a rate of about 30 ml. per minute (a fast flow of drops but not streaming). Without exposing the amalgam to air

[6] Walden, Hammett and Edmonds, *J. Am. Chem. Soc.*, **56**, 350 (1934); Lingane and Meites, *ibid.*, **69**, 277 (1947).

follow the ferric ion solution with a wash of 200 ml. of 1 *N* sulfuric acid, and then with 100 ml. of water. Remove the suction flask containing the iron solution and titrate immediately with standard permanganate solution. As usual, the end point has been reached when 1 drop of permanganate imparts a faint pink color which persists for at least 15 seconds. Calculate the percentage of iron in the ore. Duplicate determinations should show a relative deviation from the mean of 2 parts per 1000 or less.

Notes. Air must be excluded from the reductor since oxygen will react with hydrogen, which is always present in the reductor, to yield hydrogen peroxide which, in turn, reacts during the titration with permanganate: $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{++} + 5O_2 + 8H_2O$. This would cause high results for the iron analysis.

Since acid would eventually dissolve the zinc in the reductor, the amalgam should not remain indefinitely in contact with acid. When the analysis has been completed the amalgam should be washed and transferred to a jar and covered with water for storage.

Analysis of Pyrolusite

Pyrolusite, a manganese ore, is crude manganese dioxide. In this determination the indirect approach is made for the analysis. That is, a weighed amount of the sample is treated with an excess of a soluble reducing agent like sodium oxalate. The manganese dioxide oxidizes an equivalent quantity of the oxalate. The remaining oxalate is then titrated with standard permanganate solution. Knowing the total amount of oxalate added and the amount reacting with the permanganate, we may calculate the quantity of oxalate needed for reaction with the sample. With these data the percentage of MnO_2 in the ore may be calculated.

This method of analysis also may be applied to the analysis of the higher oxides of certain other metals—for example, to PbO_2, to Pb_2O_3 ($PbO_2.PbO$), and to Pb_3O_4 ($PbO_2.2PbO$). Regarding the latter two oxides of lead, it should be noted that in each case the equivalent weight is half the molecular weight since there is only one atom of lead in the plumbic valence state. Upon reacting with oxalate the plumbic lead is reduced to divalent lead; thus the whole molecule involves a gain of two electrons.

Procedure. Weigh out accurately samples of about 0.5 g. of the dry, finely divided ore and transfer to 400 ml. beakers. Calculate the weight of sodium oxalate equivalent to the sample on the assumption that the ore is pure manganese dioxide, the reaction being

$$MnO_2 + C_2O_4^= + 4H^+ \rightarrow Mn^{++} + 2CO_2 + 2H_2O$$

Weigh out accurately about 0.2 g. in excess of the calculated amount, using the same pure dry sodium oxalate as employed for standardizations, and add to the sample. Add 100 ml. of 3 *N* sulfuric acid, cover with a

watch glass and heat gently until the evolution of carbon dioxide ceases and no black particles may be seen. Do not permit the solution to evaporate too much; it may be necessary to add cautiously small amounts of water a few times to keep the volume fairly constant. Finally dilute the solution to about 250 ml., heat to 60° and titrate while hot with standard permanganate solution. Calculate the percentage of MnO_2 in the sample. Duplicate results should show a relative deviation from the mean of 4 parts per 1000 or less.

Notes. During the digestion the solution should not be allowed to evaporate to a small volume since the concentration of the solution would be increased and the temperature might climb too high with a resulting decomposition of some of the oxalic acid. Furthermore, concentrated sulfuric acid itself oxidizes oxalates.

Problem. A sample of pyrolusite (impure MnO_2) weighing 0.5000 g. was treated with 1.0000 g. of pure $Na_2C_2O_4$ and the excess was titrated with 0.1025 *N* potassium permanganate solution, 46.72 ml. being required. Calculate the percentage purity of the pyrolusite in terms of MnO_2.

Solution. It is obvious that part of the oxalate was oxidized by the MnO_2 and part by the $KMnO_4$. The g. eq. wts. of MnO_2 plus the g. eq. wts. of $KMnO_4$ must equal the g. eq. wts. of oxalate. The number of g. eq. wts. of $KMnO_4$ is $\frac{46.72}{1000}$ (0.1025). The number of g. eq. wts. of MnO_2 is $\frac{X}{43.47}$ where X is the weight of MnO_2 in grams and 43.47 is the equivalent weight of MnO_2 (half of the molecular weight). The number of g. eq. wts. of sodium oxalate is $\frac{1.0000}{67.01}$, since the equivalent weight of sodium oxalate is half of its molecular weight. Therefore

$$\frac{1.0000}{67.01} = \frac{46.72}{1000}(0.1025) + \frac{X}{43.47}$$

$$X = 0.4405 \text{ g. } MnO_2$$

and

$$\frac{100X}{0.5000} = \% \ MnO_2 = 88.1$$

Determination of Calcium[7]

The method described here may be applied to any substance of which calcium is a constituent, provided the sample is brought into solution and freed from all other cations which would precipitate insoluble oxalates. The procedure provides for the presence of magnesium and the alkali metals, but no other cations. If other cations are suspected in the sample they must first be removed. For example, if iron is present it may be removed, along with aluminum, titanium, manganese and phosphorus, by precipitation with ammonium hydroxide. Once the calcium oxalate

[7] See article by Lingane, *Ind. Eng. Chem., Anal. Ed.* 17, 39 (1945), for the volumetric determination of calcium in the presence of SiO_2, Fe, Al, Mg, P and Mn. The method is accurate and rapid.

has been precipitated from the sample it is treated with sulfuric acid, converting it into calcium sulfate and oxalic acid; the latter then may be titrated with standard permanganate solution. Thus calcium is indirectly determined in the sense that it is actually the oxalate which is oxidized by the permanganate; however, for each oxalate ion there was a calcium atom present in the original sample and the results of the titration readily may be stated in terms of calcium.

Procedure. Accurately weigh out a sample containing somewhat less than 0.1 g. of calcium (consult instructor), transfer to a 400 ml. beaker and dissolve in the smallest possible quantity of 1:1 hydrochloric acid. If effervescence occurs during solution cover with a watch glass until completely dissolved, then return any spray to the beaker by rinsing the watch glass with water. Dilute to 200 ml. (If the sample consists of the filtrate from a sample from which iron has been precipitated, begin the analysis with the filtrate containing the calcium and follow the procedure from this point on.) Add 2 or 3 drops of methyl red indicator and 5 ml. of concentrated hydrochloric acid. Heat to boiling and add a clear solution of 3 g. of ammonium oxalate dissolved in 50 ml. of warm water. With the temperature of the solution at about 75° add 1:1 ammonium hydroxide dropwise while vigorously stirring the solution. When the color changes from red to yellow stop the addition of the hydroxide. Let the beaker stand without further heating until the precipitate of calcium oxalate settles; then test for complete precipitation by adding a few drops of ammonium oxalate to the supernatant liquid. After 1 hour, and no longer if magnesium is present, filter through a paper. Wash the precipitate several times with 0.01 *M* ammonium oxalate; then dissolve the precipitate with 50 ml. of hot 1:4 hydrochloric acid and wash the paper with hot 1:100 hydrochloric acid. Dilute the solution to 200 ml., add 1 g. of ammonium oxalate dissolved in 10 ml. of hot water and heat the solution nearly to boiling. Now reprecipitate the calcium oxalate by adding ammonium hydroxide exactly as before and allow to stand an hour or even overnight. Filter through a Gooch crucible and wash the precipitate with cold water until the washings are chloride-free. Do not wash more than necessary. Place the crucible and contents in a 400 ml. beaker and add a solution of 10 ml. of concentrated sulfuric acid in 200 ml. of water. Loosen the contents of the crucible with a stirring rod and agitate until the asbestos and the precipitate are thoroughly mixed with the acid. Heat to 60° and titrate with standard permanganate solution. Calculate the percentage of CaO in the sample. Duplicate results should show a relative deviation from the mean of not more than 3 parts per 1000.

Notes. The precipitate of calcium oxalate should not be digested too long if magnesium is present since postprecipitation of magnesium oxalate may take

place. After the reprecipitation of the calcium oxalate the digestion may be extended overnight if desired, since then the concentration of magnesium ion, even if present originally in considerable amount, will be too low to cause appreciable contamination.

Though the above procedure serves well for the analysis of many substances for calcium content, it is not well adapted to the complete analysis of limestone. In order to determine silica and mixed oxides in limestone with good accuracy, a sample of 0.5 to 1 g. is required, and this would lead to an amount of calcium oxalate which would require around 100 ml. or more of 0.1 *N* permanganate in the titration. It would be possible to dissolve the calcium oxalate precipitated from a large sample of limestone and take an aliquot portion for the permanganate titration, but this would be troublesome. For the complete analysis of limestone it is customary to determine calcium gravimetrically by precipitating it and weighing as the carbonate, oxide or sulfate (see p. 267).

A rapid method of determining calcium consists of dissolving the sample and precipitating the calcium oxalate without prior removal of mixed oxides or silica. The pH of the solution is fixed at 3.7 with a formate buffer. Under these conditions calcium oxalate may be precipitated without interference from ferric or aluminum ions, and although silica is coprecipitated this does not affect the permanganate titration.[8]

Problem. A sample of 0.2008 g. of limestone was dissolved in acid, interfering ions were removed and calcium oxalate was precipitated. The precipitate was treated with sulfuric acid and titrated with 0.0990 *N* potassium permanganate, 36.22 ml. being required. Calculate the percentage of calcium present in terms of CaO.

Solution. Evidently $1CaO \simeq 1CaC_2O_4 \simeq 1C_2O_4^{=} \simeq 2e$. Therefore the equivalent weight of CaO is half of its molecular weight, or 28.04. The g. eq. wts. of $KMnO_4$ used is $\frac{36.22}{1000}(0.0990)$ and the same number of g. eq. wts. of CaO must be present. Therefore

$$\frac{36.22}{1000}(0.0990)(28.04) = 0.1005 \text{ g. CaO present}$$

$$\frac{(100)(0.1005)}{0.2008} = \% \text{ CaO} = 50.1$$

DETERMINATION OF HYDROGEN PEROXIDE

In many reactions hydrogen peroxide functions as an oxidizing agent, but in acid solution it quantitatively reduces potassium permanganate thus:

$$5H_2O_2 + 2MnO_4^{-} + 6H^{+} \rightarrow 5O_2 + 2Mn^{++} + 8H_2O$$

When the peroxide is titrated with permanganate the same initial slow fading of the color is noticed that is experienced in titrating ferrous solutions. As in the latter case the reaction proceeds rapidly from the beginning if catalyzed by adding a manganous solution.

[8] For details of this rapid method see Rieman, Neuss and Naiman, *Quantitative Analysis*, McGraw-Hill Book Co., New York, 1942, p. 394.

Procedure. Accurately weigh about 3 g. of commercial hydrogen peroxide and place in a 200 or 250 ml. volumetric flask. Dilute to the calibration mark with water and then shake. With a 25 ml. pipet measure out duplicate samples into a beaker or flask, dilute to about 100 ml., add 2 ml. of concentrated sulfuric acid dissolved in 10 ml. of water and titrate with standard potassium permanganate solution. From the relationship shown in the above equation calculate the percentage of H_2O_2 in the commercial sample. The absolute error may run as high as 0.05 per cent.

Notes. Commercial hydrogen peroxide solutions often contain small quantities of stabilizers such as acetanilide which also react with permanganate. In such a case it is preferable to determine H_2O_2 iodometrically as outlined on p. 217. In the iodometric determination the peroxide acts as an oxidant.

Peroxides of the alkali and alkaline earth metals, percarbonates and perborates may be titrated in the same way as hydrogen peroxide if they are dissolved in dilute acid.

Ceric Processes

The use of ceric ion as an oxidizing agent in volumetric analysis developed rapidly after the investigations of Willard and Young, of Furman, of Smith and others.[9] Some of the disadvantages of potassium permanganate as an oxidant have been mentioned already. Ceric sulfate has about the same oxidizing potential[10] as potassium permanganate; some ceric salts are even stronger oxidants than permanganate under similar conditions. In acid solution ceric sulfate is so stable that the normality of the solution does not change over a period of a year or more and the solution suffers no change when exposed to light. The solution is less subject than permanganate to decomposition when boiled. Ceric sulfate oxidizes reducing agents quantitatively in the presence of high concentrations of chloride ion. No intermediate products are formed during the reduction: $Ce^{++++} + e \rightarrow Ce^{+++}$. Like permanganate, ceric sulfate can serve as its own indicator since it is yellow in color, while the cerous ions are colorless. However, the color change is not so pro-

[9] Willard and Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1372 (1928); *ibid.*, **51**, 149 (1929); *ibid.*, **55**, 3260 (1933); Furman and Wallace, *ibid.*, **51**, 1449 (1929); *ibid.*, **52**, 2347 (1930); Furman, *ibid.*, **50**, 755 (1928); Kunz, *ibid.*, **53**, 98 (1931); Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191, 304 (1938); *ibid.*, **12**, 339 (1940); Part II of *Newer Methods of Volumetric Analysis*, by Oesper, D. Van Nostrand Co., New York, 1938.

[10] The oxidation potential of ceric cerium assumes different values in the presence of different anions. This may be accounted for by assuming that instead of the Ce^{++++} ion we are dealing with complex ions made up of cerium and the anion which happens to be present, e.g., $Ce(ClO_4)_6^-$, $Ce(NO_3)_6^-$, $Ce(SO_4)_3^-$ and $CeCl_6^-$. The potential associated with each complex ion would depend upon the stability of the complex. Smith and Getz, *loc. cit.*, list the following oxidation potentials for the complex ceric ions above in 1 to 8 normal solutions of the corresponding acids: 1.70 to 1.87; 1.61 to 1.56; 1.44 to 1.42; and 1.28 volts respectively.

nounced as that of permanganate and for the majority of ceric titrations the indicator "Ferroin" (see p. 184) is used. The color change, when oxidized, is from red to light blue. Ceric solutions for standardization are prepared more readily than are permanganate solutions, and it is obvious that readings of a buret filled with ceric solution may be made more easily than of one containing the darkly colored permanganate. The use of standard ceric solutions are particularly useful in potentiometric titrations where color indicators are unnecessary and where stability and high oxidizing power are important.

Preparation of 0.1 *N* Solution of Ceric Sulfate. The ceric salt most commonly used for preparing a standard solution is ceric ammonium sulfate dihydrate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$. Since only one electron is involved when the single ceric ion is reduced the molecular weight of this compound and its equivalent weight are identical, 632.6.

Procedure. Weigh out on a trip balance 64 g. of ceric ammonium sulfate and add the salt to a solution of 28 ml. of concentrated sulfuric acid dissolved in 500 ml. of water. After the salt is in solution dilute to 1 l. This solution is also approximately 1 *N* in respect to sulfuric acid. (Prove.)

Standardization. Ceric sulfate solutions may be standardized with arsenious oxide, sodium oxalate or electrolytic iron wire.

If the first of these is used the oxide is brought into solution with sodium hydroxide, the solution acidified, a catalyst and the indicator are added and the titration is carried out at room temperature. The catalytic solution is prepared by dissolving 0.25 g. of osmium tetroxide in 100 ml. of 0.1 *N* sulfuric acid. To prepare the indicator solution, Ferroin, dissolve 1.5 g. of orthophenanthroline monohydrate[11] ($C_{12}H_8N_2.H_2O$) in 100 ml. of freshly prepared 0.025 *M* ferrous sulfate solution.

Procedure. Weigh accurately 0.15 to 0.20 g. samples of pure, dry arsenious oxide and transfer to 250 ml. beakers. Add 25 ml. of 1 *N* sodium hydroxide and warm gently to hasten solution. Cool, dilute to 100 ml. and add 25 ml. of 6 *N* sulfuric acid. Add 2 drops each of osmium tetroxide and Ferroin indicator solution. Titrate with the ceric ammonium sulfate solution until the pink color changes to pale blue. Calculate the normality of the solution. A relative deviation from the mean of 1 part per 1000 should be attained.

Problem. If exactly 0.2000 g. of pure As_2O_3 is used in standardizing a ceric solution and the titration requires 40.00 ml., what is the normality?

Solution. Applying equation (1) of Chapter 6 we have:

$$N = \frac{(0.2000)(1000/40)}{197.8/4} = 0.1010$$

[11] This indicator may be purchased from G. F. Smith Chemical Co., Columbus, Ohio.

AGAINST IRON WIRE. Weigh accurately 0.18 to 0.23 g. samples of pure iron wire and place in Erlenmeyer flasks or in 400 ml. beakers. Add to each sample 10 ml. of concentrated hydrochloric acid, cover with a watch glass and heat gently until the iron has dissolved. Rinse off the watch glass. While still hot add stannous chloride solution until colorless, avoiding a large excess. Cool quickly and add 10 ml. of saturated mercuric chloride solution. A white, silky precipitate should appear; if a black or gray precipitate results metallic mercury has been formed and the experiment must be started over from the beginning. Dilute to 250 ml. with water and add 2 drops of Ferroin indicator. Titrate with the ceric ammonium sulfate solution until the color changes from pink to greenish or light yellow.

Notes. See p. 191 for preparation of the stannous chloride solution and p. 192 for a discussion of the reduction of the ferric ion.

The color change of the indicator is from pink to greenish or light yellow, instead of light blue, probably due to the presence of ferric ions.

DETERMINATION OF IRON IN AN ORE. CERIC METHOD

Read the principle and method of the iron determination as given under the permanganate method for iron, pp. 190–195. The ferric solution may be reduced by use of the Jones reductor or by the Zimmermann-Reinhardt method. In the latter, after allowing the solution to stand for 3 minutes (see p. 192), add 350 ml. of water, 20 ml. of 6 *N* hydrochloric acid, 10 ml. of 85 per cent phosphoric acid and a drop or two of Ferroin indicator. Then titrate the ferrous solution with the standard ceric ammonium sulfate until the indicator changes from pink to pale blue. Compute the percentage of iron in the ore. The precision should be as high as that obtained with the permanganate titration.

Notes. Since the ceric sulfate solution does not oxidize the chloride ion no "preventive solution" (see p. 191) is necessary. However, the phosphoric acid greatly facilitates the titration by forming the complex ferric phosphate ion, thus reducing the concentration of the ferric ion. In this way the oxidation potential of the ferric-ferrous system is sufficiently lowered to prevent the ferric ion from oxidizing the indicator before the stoichiometric point is reached.

If the reduction of the ferric solution is carried out with the Jones reductor, proceed as outlined under the permanganate method up to the point of the titration; then proceed with the titration as directed in the above section for the Zimmermann-Reinhardt method.

POTASSIUM DICHROMATE PROCESSES

Potassium dichromate has long been used as an oxidizing agent in volumetric analysis, particularly in analyzing iron ores. It is not so powerful an oxidant as permanganate, having an oxidizing potential of about 1.3 volts; this is an advantage in one sense, for it will not oxidize

chloride ion under ordinary conditions. In acid solution it reacts according to the equation

$$Cr_2O_7^{=} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$$

Its solution is stable and is easily prepared and it may be obtained in such pure form that after drying at 140° it may be weighed, dissolved and diluted to proper volume for direct use as a standard solution.[12] However, it is preferable to standardize dichromate solutions which are to be used in the analysis of iron ores or alloys against pure iron wire. With the ferrous ion it reacts as follows:

$$6Fe^{++} + Cr_2O_7^{=} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$

Until a few years ago the titration of ferrous ions with dichromate solution was hampered somewhat because the latter is not sufficiently colored to serve as its own indicator, and an external indicator had to be used. Spot tests were made from time to time as the stoichiometric point was approached by removing a drop of the titrated solution and mixing with potassium ferricyanide on a porcelain spot-plate. When the spot test no longer showed the presence of the blue precipitate of ferrous ferricyanide the oxidation of the iron was complete and the end point had been reached. However, the advent of internal oxidation indicators provided a satisfactory means of noting the end point of dichromate-iron titrations without resort to the external indicator method. Ferroin indicator has a rather high oxidation potential for use with dichromate, but diphenylamine and diphenylamine sulfonic acid are very satisfactory (see Table 17).

Preparation of 0.1 *N* Solution of Potassium Dichromate. Since there are two chromium atoms in one molecule of dichromate and each gains three electrons when acting as an oxidant, it is obvious that the equivalent weight of potassium dichromate is a sixth of its molecular weight. It follows that a liter of 0.1 *N* solution will require about 4.9 g. of the compound.

Weigh on a rough balance 4.9 g. of pure potassium dichromate, dissolve in water and dilute to 1 l. Place in a glass-stoppered bottle.

Standardization Against Iron. Accurately weigh 0.18 to 0.23 g. samples of pure iron wire and place in 250 ml. beakers or flasks. Dissolve in 10 ml. of concentrated hydrochloric acid, being careful that no loss occurs through spray. If a beaker is used, cover with a watch glass and rinse off when the iron is in solution. Add water until the volume is 25 to 30 ml. Heat almost to boiling and add stannous chloride solution drop by drop until the solution is colorless. Next add 1 drop excess, then

[12] Willard and Young, *Ind. Eng. Chem., Anal. Ed.*, 7, 57 (1935).

cool and pour in rapidly 10 ml. of saturated mercuric chloride solution. A white, silky precipitate should appear; a gray or black precipitate indicates metallic mercury, and in this case the solution should be discarded since mercury will reduce dichromate. Allow to stand 3 minutes. Add a solution of 250 ml. of water containing 5 ml. of concentrated sulfuric acid and 5 ml. of 85 per cent phosphoric acid. Add 5 drops of sodium diphenylamine sulfonate indicator (see p. 185) and titrate with the dichromate solution. The end point has been reached when a purple color first appears. Calculate the normality of the potassium dichromate solution. The relative deviation from the mean should not exceed 2 parts per 1000.

Notes. See notes on p. 192 regarding the use of stannous chloride and mercuric chloride.

Unless phosphoric acid is present the color change of the indicator occurs slowly and too soon because it is partially oxidized before the stoichiometric point is reached. The phosphoric acid prevents this by lowering the oxidation potential of the ferric-ferrous system through forming a complex with the ferric ions.

If the use of an external indicator is preferred, prepare a solution of potassium ferricyanide by dissolving a small crystal in 10 or 15 ml. of water. Place a few drops in a cup of the spot test porcelain plate and as the end point of the titration is approached transfer 1 drop of the titrated solution to the cup with a stirring rod. The appearance of Turnbull's blue (a blue precipitate) in the spot test indicates the presence of ferrous ion. Continue the titration dropwise and the spot tests until no blue precipitate is obtained within 30 seconds after adding the solution to the ferricyanide indicator.

DETERMINATION OF IRON IN AN ORE. DICHROMATE METHOD

The analysis of an iron ore by the dichromate method is carried out in every detail as described for the permanganate process except that no manganous solution is needed and an indicator is necessary. Follow the procedure beginning on p. 191 through the addition of stannous chloride and mercuric chloride. Then transfer to a 600 ml. beaker or to an Erlenmeyer flask, add a solution of 250 ml. of water containing 5 ml. of concentrated sulfuric acid and 5 ml. of 80 per cent phosphoric acid and titrate as directed above in the standardization procedure. Use diphenylamine sulfonic acid indicator or the ferricyanide external indicator. Calculate the percentage of iron in the sample. Duplicate results should check within a relative deviation from the mean of 3 parts per 1000 or better.

Problems

(See p. 217)

Chapter 12

OXIDATION AND REDUCTION IV. IODINE PROCESSES

THE STANDARD oxidation potential for the iodine-iodide system as represented by the reaction

$$I_2 + 2e \rightarrow 2I^-$$

stands roughly midway in the list in Table 17, p. 171. Therefore many systems are found with oxidation potentials lower than that of iodine-iodide, and they may be oxidized by iodine. Such reactions, when they occur quantitatively, may be applied to volumetric analysis by titrating with a standard iodine solution. They are classified under the heading of iodimetry. Among iodimetric determinations are those based upon the following reactions:

$$I_2 + H_2SO_3 + H_2O \rightarrow SO_4^{=} + 2I^- + 4H^+$$
$$I_2 + H_2S \rightarrow S + 2I^- + 2H^+$$
$$I_2 + H_2AsO_3^- + H_2O \rightarrow H_2AsO_4^- + 2I^- + 2H^+$$
$$I_2 + H_2SbO_3^- + H_2O \rightarrow H_2SbO_4^- + 2I^- + 2H^+$$
$$I_2 + Sn^{++} \rightarrow Sn^{++++} + 2I^-$$
$$I_2 + 2S_2O_3^{=} \rightarrow S_4O_6^{=} + 2I^-$$

Likewise many other systems are found with oxidation potentials higher than that of iodine-iodide, and they may be reduced by iodide with the oxidation of the latter to yield an equivalent amount of free iodine. The iodine so set free may be quantitatively determined, and thus the amount of oxidant liberating it may be computed, by titration with standard thiosulfate solution. This makes use of the last of the above reactions; such processes are classified under the heading of iodometry. Among iodometric determinations are those based upon the following reactions:

$$BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Br^- + 3H_2O$$
$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O$$
$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
$$Cr_2O_7^{=} + 6I^- + 14H^+ \rightarrow 3I_2 + 2Cr^{+++} + 7H_2O$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 5I_2 + 2Mn^{++} + 8H_2O$$
$$2Cu^{++} + 4I^- \rightarrow I_2 + 2Cu_2I_2$$
$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

Determinations based upon such reactions as are listed in the first group above are called direct determinations, because the essential constituent reacts directly with the standard (iodine) solution. In the second group of reactions we find that the essential constituent reacts to liberate iodine which, in turn, is titrated with the standard (thiosulfate) solution. The volume of thiosulfate required, and therefore the calculations involved, are exactly the same as though the essential constituent had directly oxidized the thiosulfate. The essential constituent may of course either be a component part of an unknown (copper may, for example, be determined iodometrically) or may be the primary standard used to standardize our solution (all of the first five in the second group above are ions the potassium compounds of which often are so employed for standardizing thiosulfate; copper also may be used). In this indirect manner sodium thiosulfate may be compared with a great many oxidizing substances, but it must be remembered that the direct titration of thiosulfate against oxidizing agents in general is not feasible. This is because thiosulfate is quantitatively oxidized to tetrathionate, $S_4O_6^=$, by iodine alone, in neutral or acid solution. Other oxidants practically without exception convert thiosulfate more or less incompletely to sulfate. This also is true even of iodine in weakly alkaline solutions. The proper control of the pH therefore is of first importance.

The wide use of iodimetry and iodometry in volumetric analysis is due not only to the high accuracy obtainable by these methods but also to the availability of an excellent and sensitive indicator, starch. Even with extremely small concentrations of iodine, starch gives the familiar deep blue color. The color is attributed to an adsorption complex of variable composition. The sensitivity of starch as an indicator is greater in the presence of a small amount of iodide. The sensitivity is impaired somewhat by higher temperatures and by the presence of some organic compounds such as ethyl alcohol. Starch solution should be freshly prepared or else properly preserved. In using the indicator in the titration of iodine solutions it should not be added until just before the end point is reached—that is, until the deep color of the iodine solution has changed to light amber. If the starch were added at the beginning of the titration the color of the starch-iodide complex would be practically black and there would be little or no warning as the end point was approached. Furthermore, starch adsorbs an appreciable amount of iodine from a concentrated solution which is released only slowly to a slight excess of thiosulfate. A significant error thus would result.

Preparation of Starch Indicator. Make a thin paste by stirring a little cold water with about 2 g. of soluble starch; then add about 25 ml. of cold water. Meantime boil a liter of water. Slowly pour the starch suspension into the hot water while stirring and continue to boil until

the solution is clear. Cool, add a preservative[1] if the solution is to be stored, and place in a glass-stoppered bottle. As an indicator use about 5 ml. of this solution per 100 ml. of titrated solution.

Iodimetry

Preparation of 0.1 *N* Solution of Iodine. As may be seen in the reactions given on p. 204, iodine is reduced to the iodide ion when it functions as an oxidant; therefore the equivalent weight of iodine is identical with its atomic weight. Thus to prepare a liter of 0.1 *N* solution about 13 g. of iodine is required. Iodine is not very soluble in water alone, but in an aqueous solution of potassium iodide it dissolves readily with the formation of the tri-iodide ion, I_3^-

$$I_2 + I^- \rightleftarrows I_3^-$$

When this solution reacts with a reductant the free iodine acts as the oxidant. As the iodine is used up the above equilibrium shifts to the left so that finally all of the iodine, originally present as I_2 and as I_3^-, acts in the oxidizing capacity.

Iodine solutions are not stable. They continue to decrease slightly in normality for years. Standard iodine solutions tend to hydrolyze according to the reaction

$$I_2 + H_2O = I^- + 2H^+ + IO^-$$

except in neutral or acidic solutions. In an alkaline solution the action is accelerated because of the removal of hydrogen ion to form water.

Procedure. Weigh out roughly 13 g. of resublimed iodine from a stoppered vial by difference (see p. 63), and 40 g. of potassium iodide free from iodate. Transfer the crystals of both to a 250 ml. beaker and add 25 ml. or more of water. Stir occasionally until complete solution has taken place and then pour into a glass-stoppered bottle and dilute to a liter. The solution should not be exposed to light.

Notes. If the solution is not clear after diluting, it should be filtered through asbestos in a Gooch crucible.

Test the potassium iodide for iodate by dissolving a crystal in a few milliliters of water, adding 0.5 ml. of 6 *N* sulfuric acid and 1 ml. of starch solution. If no blue color develops in 30 seconds the iodide is iodate-free ($IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$). Why is iodate objectionable here?

Standardization with Arsenious Oxide. Arsenic trioxide may be obtained well over 99.9 per cent pure As_2O_3, and after being dried at 105°

[1] Various preservatives have been suggested. Naiman, *J. Chem. Education*, **14**, 138 (1937), advocates the addition of red mercuric iodide; Nichols, *Ind. Eng. Chem., Anal. Ed.*, **1**, 215 (1929), has employed salicylic acid; Platow, *Chemist-Analyst*, June, 1939, recommends 1 g. of furoic acid per liter of starch solution. Some simply saturate the starch solution with chloroform.

it serves as an excellent primary standard for iodine solutions. After being brought into solution with sodium hydroxide ($As_2O_3 + 2OH^- + H_2O = 2H_2AsO_3^-$) the oxidation by iodine is effected during the titration according to the equation: $H_2AsO_3^- + I_2 + H_2O \rightarrow H_2AsO_4^- + 2I^- + 2H^+$. The arsenic changes valence from As^{+++} to As^{+++++} and since the trioxide contains two atoms of arsenic it is obvious that the equivalent weight of arsenic trioxide is one-fourth of its molecular weight.

Procedure. Accurately weigh samples of 0.15 to 0.22 g. of arsenic trioxide and transfer to 250 ml. Erlenmeyer flasks. Add 10 ml. of 1 *N* sodium hydroxide solution and warm until dissolved. Add 10 ml. (an excess) of 1 *N* hydrochloric acid and then carefully add a solution of sodium bicarbonate (2 g. in 50 ml. of water) until the evolution of carbon dioxide ceases. Next add about 1 g. of sodium bicarbonate to buffer the solution, dilute to 100 ml., add 5 ml. of starch indicator solution and titrate with the iodine solution until a faint blue color is obtained. Calculate the normality of the iodine solution. The relative mean deviation should be not more than 1 part per 1000.

Notes. In the titration of arsenious oxide with iodine the solution must be at a pH between 5 and 9. Below a pH of 5 the reaction is so decelerated that the end point becomes rather uncertain. The bicarbonate buffers the solution on the alkaline side.

If the highest grade of potassium iodide was used in preparing the iodine solution no blank should be necessary for the standardization, since it contains no iodate.

IODIMETRIC DETERMINATION OF SULFUR IN STEEL

Sulfur as sulfide usually is present in small amounts as an impurity in steels. It seldom exceeds 0.05 per cent. The method given here does not lead to results of highest accuracy but it is rapid and is a more or less standard procedure for steel analysis. In principle the method consists of treating the steel with acid to form hydrogen sulfide, which is passed, along with hydrogen and small amounts of other gases which are formed, into an ammoniacal solution of cadmium chloride which causes the precipitation of the sulfur as cadmium sulfide. The cadmium sulfide is acidified and the hydrogen sulfide thus regenerated is treated with standard iodine solution.

Procedure. Clean a sample of steel turnings with benzene and dry. Weigh samples of about 5 g. of the steel to the nearest hundredth of a gram. Place the sample in a 250 ml. Erlenmeyer generator flask.[2] Insert a two-hole rubber stopper and extend a thistle tube through the stopper almost to the bottom of the flask. Connect the generator flask to a second

[2] For apparatus designed especially for this determination see Scott, *Standard Methods of Chemical Analysis*, D. Van Nostrand Co., New York, 1939, p. 912; also see Steinmetz, *J. Ind. Eng. Chem.*, **20**, 983 (1928).

250 ml. flask by means of glass tubing. The glass tube should extend almost to the bottom of the second flask into which is poured 50 ml. of ammoniacal cadmium chloride solution. This solution is prepared by dissolving 5.5 g. of $CdCl_2.2H_2O$ in 50 ml. of water, adding 120 ml. of concentrated ammonium hydroxide and diluting with water to 250 ml. The flasks should be mounted in such a manner that a burner will go under the generator flask.

Through the thistle tube pour 75 ml. of 6 *N* hydrochloric acid and warm the flask with a small flame until the steel has dissolved completely; then boil gently for 1 minute, but no longer. Disconnect the receiving flask but leave the delivery tube, which may now act as a stirrer. Add 5 ml. of starch solution and 40 ml. of 6 *N* hydrochloric acid. Titrate without delay the solution of hydrogen sulfide thus formed with standard iodine solution. Calculate the percentage of sulfur in the steel.

Notes. The solution should not be boiled too long since this might cause the distillation of enough HCl to neutralize the ammonia and dissolve the cadmium sulfide.

Problem. A sample of steel weighing 5.00 g. is treated with acid and the hydrogen sulfide evolved is passed through ammoniacal cadmium chloride. The cadmium sulfide so formed is acidified and the hydrogen sulfide resulting is titrated with 0.0500 *N* iodine solution, 6.6 ml. being required. What is the percentage of sulfur in the steel?

Solution. The number of g. eq. wts. of iodine used is $\frac{6.6}{1000}$ (0.0500), and the same number of g. eq. wts. of sulfur must be present. Therefore, since the g. eq. wt. of sulfur is $^{32}/_{2}$ or 16 (see the equation, p. 204, showing that the electron shift for the sulfur atom is 2), we have

$$\frac{(0.0066)(0.0500)(16)(100)}{5.00} = \%\,S = 0.11$$

DETERMINATION OF ANTIMONY IN STIBNITE

Stibnite is an ore consisting largely of antimony sulfide, Sb_2S_3, and some silica. The following procedure is not suitable for ores containing appreciable amounts of arsenic or of iron which cause errors unless they are first separated from the antimony. The principle involved in the iodimetric determination of antimony is essentially the same as in the standardization of an iodine solution with arsenic trioxide. Antimony, like arsenic, may be oxidized from a valence of 3^+ to 5^+ and the essential reaction of the titration may be seen on p. 204. Actually, because tartaric acid is added during the course of the analysis, the reaction is: $H(SbO)C_4H_4O_6 + I_2 + H_2O = H(SbO_2)C_4H_4O_6 + 2I^- + 2H^+$. The titration is quantitatively complete only if the solution is neutral or slightly alkaline; if the pH is too low iodide reduces antimonate, while if too high the reaction between iodine and water ($I_2 + H_2O = I^- + IO^- + 2H^+$)

is driven to the right because the hydroxyl ions remove the hydrogen ions. In the presence of sodium bicarbonate the reaction proceeds satisfactorily. Provision also must be made to prevent loss of antimony chloride by volatilization when the ore is being dissolved in hydrochloric acid. This is accomplished by careful control of the temperature and by the addition of potassium chloride which increases the chloride ion concentration, and this, in turn, increases the concentration of the complex ion, $SbCl_4^-$.

It is also necessary when the solution is diluted to prevent the precipitation of basic antimony chloride, SbOCl, which may be formed by hydrolysis. Hydrolysis may be prevented, however, by controlling the acidity and by forming a complex antimony tartrate as already mentioned.

Procedure. Accurately weigh out samples of the finely divided, dry ore of about 0.5 to 1 g. each. Transfer to 400 ml. beakers and add 20 ml. of concentrated hydrochloric acid and 0.3 to 0.4 g. of potassium chloride. Cover with a watch glass and heat on a steam bath for 15 minutes or until the residue of silica is white. Add 3 g. of tartaric acid and heat on the steam bath for 10 minutes longer. Slowly add, with constant stirring, 100 ml. of cold water. Should a red precipitate of antimony sulfide appear at this point it indicates that hydrogen sulfide was not completely expelled. In that case, stop the addition of water, heat the solution again over the steam bath until the precipitate dissolves; then cool and add the remaining part of the 100 ml. of cold water. Should a white precipitate of basic antimony chloride appear when the solution is diluted it will be necessary to start over from the beginning, since it is practically impossible to bring the basic salt back into solution. Add 4 drops of methyl red indicator and 6 *N* sodium hydroxide solution until the solution has just turned yellow; then add 6 *N* hydrochloric acid, drop by drop, until the solution is barely acid, i.e., faintly pink or orange. After this add 3 g. of sodium bicarbonate in 100 ml. of water, and 5 ml. of starch solution. Then titrate with standard iodine solution. The approach to the end point should be made with utmost care since the reaction between trivalent antimony and iodine is relatively slow and the end point might easily be overrun. Calculate the percentage of antimony in the ore. The relative mean deviation might run as high as 3 or 4 parts per 1000.

THE DETERMINATION OF ANTIMONY IN TARTAR EMETIC

This substance, $KSbC_4H_4O_6.\frac{1}{2}H_2O$, is used in medicine to cause emesis. Since one molecule of the compound contains one atom of trivalent antimony the analysis may be carried out essentially as outlined for stibnite.

Procedure. Weigh accurately samples of 0.5 to 0.6 g. Add 100 ml. of water to dissolve, then about 1 g. of tartaric acid and 2 g. of sodium bicarbonate. Put in 5 ml. of starch solution and titrate with standard iodine solution. Calculate the percentage purity of the salt. The relative mean deviation should not exceed 2 parts per 1000.

Iodometry

Preparation and Standardization of 0.1 *N* Sodium Thiosulfate. Any substance which meets the criteria of primary standards in general (p. 78) and which quantitatively oxidizes iodides to iodine may be used to standardize a solution of sodium thiosulfate. The substances most commonly used are the potassium salts of bromate, iodate and dichromate. The bi-iodate also often is used. Metallic copper may be employed since cupric salts react with iodide in weakly acid solution to liberate iodine, but this method is recommended only when the thiosulfate solution is to be used for the determination of copper. Whatever standard is selected, the accurately weighed substance reacts in an acid solution of potassium iodide to set free a definite quantity of iodine which then is titrated with the thiosulfate solution the normality of which is sought: $2S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2I^-$. If the bromate or iodate is used as the standard it is evident that no colored product is formed save the iodine itself, with the result that the titration with thiosulfate, using starch as the indicator, gives a color change at the end point from blue to colorless. On the other hand, if potassium dichromate is used as the standard, the greenish chromic ion is formed in the reaction with the iodide ion. Thus when the solution is titrated with thiosulfate the color change at the end point is from blue to light green. This is sometimes mentioned as a disadvantage to the use of dichromate as the standard. As a matter of fact, unless one is partially color-blind this presents not the slightest difficulty, and because of other advantages (e.g., the equivalent weight of potassium dichromate is greater than that of any of the other three) it is preferred by many analysts over other primary standards.

Before taking up the actual procedure for making up and standardizing a solution of sodium thiosulfate let us examine the reactions between iodides and bromates and between iodides and iodates. The equation for the former reaction is

$$(1) \qquad BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Br^- + 3H_2O$$

The iodide ions lose one electron each to become iodine atoms, or molecules; at the same time the bromate ion is reduced to bromide ion, and this involves a gain of six electrons. It is obvious then that the equivalent weight of potassium bromate is its molecular weight divided by 6, or 167.01/6 = 27.84.

Consider now the corresponding reaction between iodate and iodide ions. The equation is sometimes written (in a manner analogous to the bromate reaction)

$$IO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + I^- + 3H_2O \quad (2)$$

However, here we have iodide ion appearing on both sides of the equation; it obviously may be condensed to read

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (3)$$

According to equation (2) the equivalent weight of potassium iodate would be one-sixth of its molecular weight, but noting in equation (3) that 5 iodide ions are oxidized, we conclude that the equivalent weight of the iodate is one-fifth of its molecular weight.

Though we might expect bromate and iodate to act alike there is no anomaly here. It ought to be evident that if the same number of moles of potassium iodate and potassium bromate were weighed out, acidified and titrated directly with potassium iodide solution (electrometrically, for since the iodine color appears immediately the color indicator, starch, could not be used to mark the end point), $\frac{6}{5}$ more iodide solution would be necessary in the bromate titration than in the iodate titration. This is mathematically evinced by equations (1) and (3). Or sometimes it is reasoned as follows, though such reasoning is arguing in circles: "The iodate ion is reduced to iodide ion as equation (2) implies, but it could never remain in solution as such, since more iodate would oxidize it, the iodide, to iodine. This means that just that much less iodide would have to be added from the buret to satisfy the needs of the given weight of iodate." This reasoning automatically leads to the conclusion that equation (3) is the correct representation and not equation (2). Though the conclusion is right the fallacy of such reasoning is that it assumes that iodine in the iodate would pass from a valence of 5^+ to a valence of 1^- in iodide, and then return to a valence of zero in molecular iodine. It is only logical to say that the iodate ion is reduced directly to I^0 while, simultaneously, iodide ion (from the buret) is oxidized to I^0.

Of course the chief objection to writing the equation as expressed in (2) is that it leads to the erroneous conclusion that the equivalent weight of potassium iodate, when titrated with potassium iodide, is one-sixth of the molecular weight, whereas actually it is one-fifth. (Note, however, that equation (1) shows that if potassium bromate is titrated with potassium iodide, the equivalent weight of the bromate *is* one-sixth of its molecular weight. The reduction of bromate by iodide could not possibly stop at the elementary bromine state since bromine is reduced by iodide to bromide.)

Nothing that has been said above belies the fact that, used as a primary standard in the standardization of sodium thiosulfate solution, the equivalent weight of potassium iodate is one-sixth of its molecular weight, just as is the case with potassium bromate. Consider again equations (1) and (3); in both instances one mole of the halate liberates three moles of iodine ($3I_2$). Therefore, when the iodine is titrated with thiosulfate

$$3I_2 + 6S_2O_3^- \rightarrow 3S_4O_6^- + 6I^-$$

the same amount of thiosulfate is required. In brief, a mole of either bromate or iodate gives rise to that quantity of iodine which oxidizes six moles of thiosulfate. Each molecule of thiosulfate when oxidized loses one electron. It follows then that the equivalent weight of both potassium bromate and potassium iodate, when

used in iodometry, is one-sixth the molecular weights. The fact that potassium iodate has an equivalent weight which sometimes is one-fifth and sometimes one-sixth of its molecular weight should remind us of a statement made earlier (p. 153) that "it is imperative that one consider the particular reaction which the reagent is undergoing . . . before deciding what is the equivalent weight."

Sodium thiosulfate solution is very difficult to prepare in such a manner that it will maintain a constant normality. Often the concentration will vary significantly even within a period of one or two days. The change in normality may be either positive or negative. Oxidation by atmospheric oxygen may occur:

$$2S_2O_3^{=} + O_2 \rightarrow 2SO_4^{=} + 2S$$

which may account for a decrease in normality. The bacterium, *Thiobacillus thioparus*, which is said to be ordinarily present in air,[3] slowly decomposes the solution. The gain in normality may be explained as a result of acidity, possibly due to the presence of carbon dioxide:

$$S_2O_3^{=} \xrightarrow{H^+} SO_3^{=} + S$$

Thus for each thiosulfate ion lost there is a gain of one sulfite ion, and since the latter ion has twice the reducing capacity of the thiosulfate ion (gaining two electrons when oxidized to $SO_4^{=}$ as compared with one electron gained by $S_2O_3^{=}$ in iodometry), the net result is an increase in the normality of the solution as a reductant. To overcome these difficulties a great many suggestions have been made. Boiling the water in which the thiosulfate is to be dissolved destroys the bacteria and also expels carbon dioxide. Of course the storage bottle and its stopper should be sterile. Sodium carbonate, borax, sodium furoate and chloroform have been used as preservatives.

Procedure. Weigh out approximately 25 g. of sodium thiosulfate pentahydrate and transfer to a liter Pyrex bottle which has been sterilized with hot water. Boil a liter of distilled water and pour while quite hot into the bottle. Plug the mouth of the bottle with sterile cotton while the solution cools, then add as a preservative either 2 g. of borax, 0.5 g. of sodium carbonate, 1 g. of sodium furoate or several drops of chloroform. Stopper the bottle and shake.

Standardization with Potassium Dichromate. The reaction between the dichromate and iodide ions in an acid medium

$$Cr_2O_7^{=} + 6I^- + 14H^+ \rightarrow 3I_2 + 2Cr^{+++} + 7H_2O$$

requires a rather high acidity if it is to proceed rapidly. The standardization can be carried out at a lower acidity if air is expelled from the flask

[3] Kassner and Kassner, *Ind. Eng. Chem., Anal. Ed.*, **12**, 655 (1940).

with carbon dioxide, thus avoiding the danger of oxidation of iodide by air, which may happen in strongly acid solutions.[4]

Procedure. Accurately weigh out samples of about 0.2 g. (confirm this value) of pure potassium dichromate which has been well dried at 140°, and dissolve in 40 to 50 ml. of water. Add 8 ml. of concentrated hydrochloric acid. Meantime, fill the buret with the thiosulfate solution which is to be titrated and set the meniscus on the zero mark. Prepare the starch indicator solution if this has not already been done. Next quickly dissolve about 3 g. of pure potassium iodide in 10 or 15 ml. of water, add it immediately to the acidified dichromate solution, dilute to about 150 ml. and stir. Set in a dark place for 3 minutes only and then titrate with thiosulfate, stirring constantly, until the dark amber color gives way to an orange-green. Then add 5 ml. of starch indicator and slowly continue the titration until the blue color suddenly is replaced by a clear, light green. Run a blank using the same quantities of all reagents except potassium dichromate. Calculate the normality of the thiosulfate solution. The relative mean deviation should not exceed 1 part per 1000.

Notes. The potassium iodide solution should not be prepared until everything else is in readiness because the solution will throw out iodine if allowed to stand in the light and exposed to air even for a few minutes. After bringing the solutions of potassium iodide and acidified potassium dichromate together they should be placed in the dark for 3 minutes to allow time for them to react quantitatively. Too long a period, though, may result in loss of iodine through volatilization or a gain in iodine by oxidation ($4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O$), either of which would introduce an error into the titration which follows.

The solution should be stirred or swirled constantly while titrating in order to prevent the reaction, $S_2O_3^- \xrightarrow{H^+} SO_3^- + S$, due to a local excess of thiosulfate in the acid solution.

A blank run is necessary if the potassium iodide crystals contain small amounts of the oxidant, potassium iodate.

Standardization with Potassium Bromate, Iodate or Bi-iodate. Because the equivalent weights of these three standards are not widely different, being respectively 27.84, 35.67 and 32.50 (confirm), about the same amount of any may be used in the standardization of thiosulfate. The manner in which they react with potassium iodide has already been explained (p. 210).

Procedure. Accurately weigh out samples of about 0.10 to 0.12 g. of pure, dry potassium bromate, potassium iodate or potassium bi-iodate and dissolve in 40 to 50 ml. of water. Add 8 ml. of concentrated hydrochloric acid. Fill the buret with the thiosulfate solution which is to be standardized and set the meniscus on the zero mark. Prepare the starch

[4] Bray and Miller, *J. Am. Chem. Soc.*, **46**, 2204 (1924); Popoff and Whitman, *ibid.*, **47**, 2259 (1925); Hahn, *ibid.*, **57**, 614 (1935).

indicator solution if this has not already been done. Next quickly dissolve about 3 g. of pure potassium iodide in 10 or 15 ml. of water, add it immediately to the acidified solution of the bromate (or iodate or biiodate), dilute to about 150 ml. and stir. Set aside in a dark place for about 3 minutes and then titrate with the thiosulfate until the solution is light amber in color. Add 5 ml. of starch indicator and slowly continue the titration until the blue color gives way to colorless. Run a blank using the same quantities of all reagents except the oxidant, which is omitted. Calculate the normality of the thiosulfate solution. The relative mean deviation should not exceed 1 part per 1000.

Notes. Read the notes following the procedure for standardizing the solution with potassium dichromate.

Standardization with Copper. Copper is recommended as a primary standard for thiosulfate only when the latter is to be used for the determination of copper. Under proper conditions copper ions oxidize iodide ions quantitatively:

$$2Cu^{++} + 4I^- \rightarrow Cu_2I_2\downarrow + I_2$$

and the liberated iodine may be titrated with thiosulfate. A weighed quantity of copper is dissolved in nitric acid. The excess nitric acid and oxides of nitrogen are expelled by evaporation with sulfuric acid. Then the pH is adjusted to about 3.7 and the solution titrated.

The oxidation-reduction represented by the above equation takes place despite the fact that the oxidation potential of the iodine-iodide system is above that of the cupric-cuprous system (see Table 17, p. 171). This is accomplished by keeping the concentration of cuprous ion at a very small value since cuprous iodide is precipitated, and by making the concentration of the iodide ion quite large through adding a considerable excess of potassium iodide.

The end point in this titration is not difficult to recognize but is somewhat unusual in that the precipitate of cuprous iodide is present. This precipitate adsorbs a quantity of iodine, insufficient to affect appreciably the results of the standardization, but sufficient to change the normally white cuprous iodide to a cream or ivory color. The color change at the end point, therefore, is not from blue or lavender to white but from lavender to ivory.

Procedure. Accurately weigh samples of clean, bright copper wire of about 0.2 to 0.25 g. each. Place the copper in a casserole and add 5 ml. of concentrated nitric acid and allow to dissolve. If necessary add another 5 ml. of nitric acid. When dissolved add 2 ml. of concentrated sulfuric acid and evaporate carefully over a very low flame until sulfuric acid fumes appear. Avoid spattering. Cool and very cautiously add 25 ml. of

water, and then slowly add 6 *N* ammonium hydroxide until the solution barely attains a deep blue color. Next add 20 ml. of 6 *N* acetic acid. The solution should now have a pH of about 3.7. Dissolve 3 g. of pure potassium iodide in 10 or 15 ml. of water and add at once to the copper solution. Titrate the liberated iodine with the thiosulfate solution until the muddy brown color has almost faded; then add 5 ml. of starch solution and complete the titration. Calculate the normality of the thiosulfate solution. The relative mean deviation should not exceed 2 parts per 1000.

IODOMETRIC DETERMINATION OF COPPER IN AN ORE

The analysis of a substance which contains no interfering elements may be carried out by essentially the same procedure as has been given for the standardization of thiosulfate with metallic copper. But many ores of copper contain, besides silica, such metallic impurities as aluminum, iron, silver, arsenic and antimony. Silver and aluminum cause no trouble in the analysis for copper, but ferrous iron, trivalent arsenic and antimony do interfere because they act as reductants. Ferric iron cannot be tolerated since it acts as an oxidant. Although pentavalent arsenic and antimony react with the iodide ion, they do so only slowly under the proper condition of acidity (pH > 3.5), and their presence causes no serious error. The ore is brought into solution with nitric acid or with aqua regia and the oxides of nitrogen are expelled by evaporation with sulfuric acid, for they would oxidize iodide if allowed to remain in solution. Any arsenic or antimony is oxidized to the harmless pentavalent state with bromine and the excess bromine is eliminated by boiling. The acidity is fixed at a pH around 3.7 and the iron, which was oxidized to the ferric state by bromine, is decreased to a negligible concentration of ferric ion by converting it into the complex $FeF_6^{=}$ ion with ammonium bifluoride. The solution then may be treated with excess potassium iodide and the iodine liberated by the cupric ion titrated with the standard thiosulfate solution.

Procedure. Accurately weigh samples of the finely divided, dry ore of about 0.5 g. or more and transfer to 250 ml. beakers. Add 10 ml. of concentrated nitric acid and heat over a very low flame until all that remains undissolved is a white siliceous residue. If solution of the copper is incomplete, add 5 ml. of concentrated nitric acid and 5 ml. of concentrated hydrochloric acid, heat the solution and cool. Add 5 ml. of concentrated sulfuric acid. Heat cautiously over a hot plate until sulfuric acid fumes are evolved. Cool and very carefully add 25 ml. of water. If the residue is white it need not be filtered; if dark, filter and wash residue and filter paper thoroughly.

When the copper is in solution add 5 ml. of saturated bromine water

and boil gently for several minutes to expel the excess bromine. (Test vapors for bromine with starch-iodide paper prepared by dipping a piece of filter paper in a solution of starch and potassium iodide.) Cool the solution, add 6 *N* ammonium hydroxide until a faint permanent precipitate of ferric hydroxide has been obtained, or in the absence of iron. until, after stirring, a slight odor of ammonia persists. Then add 20 ml. of 6 *N* acetic acid. Test the solution with hydrion paper by touching the paper to the stirring rod in the beaker. If the pH is not about 3.7, adjust by adding a few drops of acetic acid or of ammonium hydroxide. Add 2 g. of ammonium bifluoride. Stir until dissolved and then add a freshly prepared solution of 3 g. of potassium iodide in 10 or 15 ml. of water. Titrate the liberated iodine at once with the standard thiosulfate solution, using starch indicator after the muddy brown color has changed to very light brown. Continue adding thiosulfate drop by drop until the lavender color changes to ivory. If desired, 2 g. of ammonium thiocyanate may be added just before the end point; this reduces the amount of iodine adsorbed by the precipitate (see discussion under Standardization with Copper, p. 214) and causes a sharper end point.[5] Run a blank and make the necessary correction. Calculate the percentage of copper in the ore. The relative mean deviation should not exceed 3 parts per 1000.

Notes. After the end point is reached no blue color should return for at least 10 minutes. An almost immediate return of color indicates too much ammonium hydroxide or too little bifluoride, or oxides of nitrogen.

DETERMINATION OF AVAILABLE CHLORINE IN BLEACHING POWDER

Bleaching powder has the formula Ca(OCl)Cl. The compound is capable of reacting with acids to liberate chlorine.

$$CaOCl_2 + 2H^+ \rightarrow Ca^{++} + Cl_2 + H_2O$$

As a bleaching agent or a disinfectant the value of bleaching powder depends upon the amount of chlorine which it makes "available." If bleaching powder is allowed to react with an excess of potassium iodide it liberates free iodine,

$$OCl^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

which then may be titrated with standard thiosulfate solution.

Procedure. Accurately weigh out to the third decimal place about 5 g. of commercial bleaching powder and grind it in a mortar, adding small quantities of water and grinding thoroughly after each addition until the powder becomes a smooth paste. Wash the contents of the mortar quantitatively into a 500 ml. volumetric flask and dilute to the mark with water.

[5] Foote and Vance, *J. Am. Chem. Soc.*, **57**, 845 (1935); *Ind. Eng. Chem., Anal. Ed.*, **8**, 119 (1936).

Shake the suspension well and transfer 50 ml. portions by means of a pipet to 250 ml. conical flasks, observing the precaution that the liquor withdrawn contains in each case its proportion of suspended matter. Dilute the 50 ml. portions to 100 ml., add a freshly prepared solution of 3 g. of potassium iodide in 10 ml. of water, and 10 ml. of 6 *N* sulfuric acid. Titrate the liberated iodine with standard thiosulfate solution, adding 5 ml. of starch indicator solution just before the end point. Calculate the percentage of available chlorine. Duplicate results should agree within a relative mean deviation of 1 part per 1000 if the volumetric flask is well shaken before removing the aliquot portions with the pipet.

DETERMINATION OF HYDROGEN PEROXIDE

The reaction of hydrogen peroxide and potassium iodide in the presence of acid proceeds according to the equation,

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

and though it proceeds slowly it may be catalyzed by the molybdate ion. The iodine liberated is titrated with standard thiosulfate solution.

Procedure. A sample of commercial hydrogen peroxide is diluted in a volumetric flask in the manner described in the procedure for analysis by the permanganate method, p. 199. Pipet aliquot portions of 25 ml. into 125 ml. conical flasks, acidify with 8 ml. of 6 *N* sulfuric acid, add a freshly prepared solution of 3 g. of potassium iodide dissolved in 10 ml. of water and 3 drops of neutral 1 *N* ammonium molybdate solution. Titrate the liberated iodine with standard thiosulfate solution, adding 5 ml. of starch indicator solution just before the end point is reached. Prove from the equations involved that 1 ml. of tenth-normal thiosulfate solution is equivalent to 0.001701 g. of hydrogen peroxide. Calculate the percentage of H_2O_2 in the sample. The deviation from the mean may be as high as 4 parts per 1000.

Problems

1. A solution contains 6.355 g. of $KHC_2O_4.H_2C_2O_4.2H_2O$ per 100.0 ml. (a) What is its molarity? (b) What is its normality as an acid? (c) What is its normality as a reducing agent?
   Answer: (a) 0.2500; (b) 0.7500; (c) 1.000.
2. Exactly 40.00 ml. of a KHC_2O_4 solution is equivalent to 25.00 ml. of a potassium hydroxide solution which contains 11.22 g. of KOH per liter. How many milliliters of acidified potassium permanganate solution containing 10.54 g. of $KMnO_4$ per liter will react with 30.00 ml. of the oxalate solution?
   Answer: 22.49 ml.
3. A solution contains 9.488 g. of $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$ per 50.00 ml. If a stannous tin solution is oxidized by 35.36 ml. of the ceric solution, how many grams of tin are present?
   Answer: 0.6296 g.

4. Fifty ml. of a solution of potassium dichromate containing 25.00 g. of $K_2Cr_2O_7$ per liter is acidified with sulfuric acid and poured into 140.0 ml. of ferrous ammonium sulfate hexahydrate containing 100.0 g. of $FeSO_4.(NH_4)_2SO_4.6H_2O$ per liter. Does the resulting solution contain excess oxidizing or reducing agent? How many milliliters of 0.4000 *N* oxidizing or reducing solution will be required in order that no excess of oxidant or reductant be present?
   Answer: 25.53 ml. of oxidant.
5. Calculate the normality of a solution of potassium permanganate of which 38.46 ml. is necessary to react with 0.2698 g. of sodium oxalate.
   Answer: 0.1047 *N*.
6. The potassium permanganate solution of problem 5 has what arsenious oxide value; i.e., what weight of As_2O_3 is equivalent to 1.000 ml. of the permanganate?
   Answer: 0.005178 g.
7. Calculate the normality of a ceric ammonium sulfate solution of which 33.33 ml. is found to be equivalent to 0.1948 g. of pure iron wire.
8. What is the normality of a sodium thiosulfate solution of which 40.42 ml. reacts with the iodine set free from excess potassium iodide by 0.1177 g. of potassium bromate?
9. The sodium thiosulfate of problem 8 above has what potassium bi-iodate value?
   Answer: 0.003399 g.
10. Calcium oxalate is precipitated from a 0.3608 g. sample of limestone containing 41.75 per cent CaO. The precipitate is treated with excess sulfuric acid and titrated with a potassium permanganate solution, 42.52 ml. being required. Calculate the molarity of the permanganate solution.
   Answer: 0.02526 *M*.
11. Approximately 5 ml. of a hydrogen peroxide solution is found to weigh 5.162 g. It is titrated with a 0.1050 *N* potassium permanganate solution. The buret reading is 40.02 ml. Calculate the percentage of H_2O_2 in the sample.
   Answer: 1.39%.
12. A potassium permanganate solution is of such concentration that 1.000 ml. of it is equivalent to 0.002900 g. of potassium bromate. One ml. of a second permanganate solution is equivalent to 0.01000 g. of arsenious oxide. How many milliliters of the first permanganate solution must be added to 100.0 ml. of the second permanganate solution in order that the resulting normality will be 0.1500?
   Answer: 114.0 ml.
13. A certain volume of a potassium dichromate solution will oxidize a weight of potassium tetroxalate, $KHC_2O_4.H_2C_2O_4.2H_2O$, which requires four-tenths of that volume of 0.2500 *N* sodium hydroxide for neutralization. If this same potassium dichromate solution is used to analyze an iron ore, and 40.20 ml. is necessary in the titration of the ferrous solution from a 1.5000 g. sample of the ore, what is the percentage of iron in terms of Fe_2O_3?
   Answer: 28.53%.
14. A sample of pyrolusite, impure MnO_2, weighing 0.6022 g. is treated with an excess of hydrochloric acid and the chlorine which is evolved is passed into a potassium iodide solution. The iodine thus liberated is titrated with a sodium

thiosulfate solution (of which 1 l. is equivalent to 12.71 g. of copper), 41.56 ml. being used. Calculate the percentage of MnO_2 in the pyrolusite.

Answer: 60.01%.

15. The MnO_2 in a sample of pyrolusite, crude MnO_2, is equivalent to 22.02 ml. of sodium thiosulfate (1.000 ml. of which reduces the iodine liberated from potassium iodide by 0.005025 g. of potassium dichromate). The sample is treated with a weighed excess of sodium oxalate, in the presence of sulfuric acid, and titrated with 0.1009 *N* potassium permanganate solution. If 32.25 ml. of the permanganate solution was used, what weight of sodium oxalate must have been added?

Answer: 0.3692 g.

16. Calculate the weight of potassium iodate necessary to liberate that amount of iodine from potassium iodide which will react with 45.67 ml. of a sodium thiosulfate solution, 38.24 ml. of which is equivalent to 40.20 ml. of an iodine solution, if 45.67 ml. of the iodine solution is equivalent to 0.2420 g. of antimony trioxide.

Answer: 0.1245 g.

17. A 0.5000 g. sample of chromite ore (crude $FeO.Cr_2O_3$) is fused with sodium peroxide, acidified, and the resulting chromate solution is divided into two equal parts. One portion is analyzed for chromium by adding to it 40.00 ml. (an excess) of freshly prepared, pure ferrous sulfate solution containing 5.560 g. of $FeSO_4.7H_2O$ per 100.0 ml.; 22.42 ml. of potassium dichromate solution (1.000 ml. is equivalent to 0.005000 g. of pure iron) is required to titrate the excess ferrous sulfate. (a) Calculate the percentage of chromium in the ore. (b) The other portion is added to excess potassium iodide. How many milliliters of sodium thiosulfate will be necessary to titrate the liberated iodine if 1.000 ml. of thiosulfate is equivalent to 0.01222 g. of Cu?

Answer: (a) 41.55%; (b) 31.16 ml.

18. A solution contains only sulfuric acid, chromic acid and water. Exactly 1 g. is diluted and titrated with 0.1100 *N* ferrous sulfate solution, 38.50 ml. being required. Another 1 g. sample is titrated with 0.1525 *N* sodium hydroxide solution for total acidity; 48.20 ml. of the base is necessary. Calculate the percentage of each acid present.

Answer: 16.66% H_2CrO_4; 22.20% H_2SO_4.

19. Thirty ml. of potassium permanganate solution which has been standardized against sodium oxalate and found to be 0.1000 *N* is added to an excess of manganous sulfate with which it reacts thus:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

Calculate the number of milliliters of 0.05000 *N* sodium hydroxide solution which will be needed to neutralize completely the solution resulting after the above reaction.

Answer: 24.00 ml.

20. A manganese ore weighing 0.1856 g. was brought into solution with the manganese in the Mn^{++} state. It was titrated in neutral solution with standard potassium permanganate solution:

$$3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$$

The titration required 48.20 ml. of permanganate. The permanganate, as standardized against sodium oxalate in acid solution, has a normality of 0.1111. Calculate the percentage of manganese in the ore.

Answer: 47.6%.

21. A sample weighing 0.2500 g. and consisting entirely of Fe and Fe_3O_4 is dissolved, reduced completely to ferrous iron and titrated with 0.1000 *N* ceric ammonium sulfate solution, 40.00 ml. being required. Calculate the percentages of Fe and Fe_3O_4 in the sample.

Answer: 61.5% Fe; 38.5% Fe_3O_4.

22. In calculating the normality of an oxidizing solution which was standardized against oxalate, an analyst used the equivalent weight of potassium oxalate and obtained 0.0782 as the normality. He then discovered that actually sodium oxalate had been used. What is the correct normality of the oxidizing solution?

Answer: 0.0970 *N*.

23. How many grams of sulfur dioxide will be needed to destroy the odor caused by hydrogen sulfide in one cubic meter of water:

$$SO_2 + 2H_2S = 3S + 2H_2O$$

if it is found that 1 l. of the water, when treated with 40.00 ml. (an excess) of 0.1000 *N* iodine solution, requires 19.84 ml. of 0.1092 *N* sodium thiosulfate solution to titrate the excess iodine?

Answer: 29.4 g.

24. The sulfur occurring as sulfide in a 5.00 g. sample of steel is determined as outlined on p. 207, except that the hydrogen sulfide is passed into an excess of standard iodine solution and the iodine remaining after reaction with the hydrogen sulfide is titrated with standard sodium thiosulfate solution. The volume of iodine solution receiving the hydrogen sulfide was 20.00 ml. and the thiosulfate necessary for the titration was 18.06 ml. One ml. of the iodine solution is equivalent to 0.990 ml. of the thiosulfate solution and 1.000 ml. of the latter is equivalent to 0.00536 g. of Cu_2O. Calculate the percentage of sulfur in the steel.

Answer: 0.042%.

25. A sample of potassium iodide of commercial grade weighing 0.3893 g. is dissolved in water and added to an acidified solution of 0.1141 g. of pure potassium bromate. The solution is boiled gently until all of the liberated iodine is expelled. It then is cooled and an excess of reagent potassium iodide is added, after which it is titrated with 18.02 ml. of sodium thiosulfate solution of which 1.000 ml. is equivalent to 0.003567 g. of potassium iodate. Calculate the purity of the commercial potassium iodide.

Answer: 98.0%.

Chapter 13

GRAVIMETRIC ANALYSIS. FUNDAMENTAL PRINCIPLES

Gravimetric analysis includes those determinations in which the constituent sought is isolated and weighed. The constituent may be separated from other components in the original sample in the form of the constituent itself or as one of its compounds. The electrodeposition of copper on the cathode during the electrolysis of one of its soluble compounds illustrates the former. The latter type is illustrated by the determination of carbon dioxide from a carbonate sample in which the gas is trapped after evolution in an absorbent such as sodium hydroxide, and weighed. By far the most common type of gravimetric analysis, however, is that in which the essential constituent is converted into a difficultly soluble compound which is filtered, washed, dried and weighed. In this last case it is imperative that the compound which is precipitated be thrown out of solution quantitatively, which is to say it must be practically insoluble. It should be a substance which presents no particular difficulty in filtering and washing. It must be a compound of definite composition or must be converted into a compound of definite composition in a simple manner, as by ignition, in order that its weight may have a known mathematical relationship to the original sample.

The Solid State

The formation of a precipitate consists of throwing a substance out of solution and into the solid state. A true solid is a substance which has assumed a crystalline form in which the ions of the compound are arranged in some symmetrical fashion about an imaginary three-dimensional trellis known as the crystal lattice. There are strong forces which keep the ions in their orderly arrangement in the lattice, forces which must be overcome in order to disrupt the architecture of the crystal. This may be done by a sufficiently high temperature (melting or sublimation) or by dissolving in some solvent. In the latter case obviously there is an attraction between the ions of the crystal and those in the solution which is greater than the intracrystalline forces. The extent of solubility of a given compound in a given solvent must depend upon the relative magnitudes of the two forces. It is not surprising, then, that solubility

should vary so widely for different compounds in a given solvent or for the same compound in different solvents. Nor should one expect solubility to be independent of temperature since the kinetic energy of molecules and ions varies with a change in temperature. A saturated solution, being one in which the solution is in equilibrium with the solute, is a solution in which the attractive forces, between ions within the crystal and between ions of the crystal and of the solution, are equal. When this equality has been established the rate at which ions are leaving the crystal lattice is equal to the rate of deposition of ions from the solution upon the lattice.

Solubility Product. The equilibrium between a salt and its saturated solution may be studied from the standpoint of the Law of Mass Action. When the solid, BA, is dissolved in water, sooner or later the solution becomes saturated and the equilibrium may be expressed by the equation

$$\underset{\text{(solid)}^1}{BA} \rightleftarrows \underset{\text{(solution)}}{B^+ + A^-} \tag{1}$$

It will be recalled that the Law of Mass Action states that for equilibria in general the equilibrium constant is equal to the product of the concentrations of the ions or molecules on the one side of the equation divided by the product of the concentrations on the other side, all raised to a power represented by the coefficients of the ions or molecules. Thus the mass law expression for the above reaction is simply

$$\frac{[B^+][A^-]}{[BA]} = K \tag{2}$$

Since solid is present and the solution is saturated the value of [BA] is constant and the denominator may be combined with K, yielding

$$[B^+][A^-] = K_{s.p.} \tag{3}$$

where $K_{s.p.}$ is known as the solubility product.[2] The solubility product of a salt of a two-one valence type, for example B_2A, is, of course

$$[B^+]^2[A^-] = K_{s.p.} \tag{4}$$

The solubility of any salt is measured by the concentration of the saturated solution. Assuming that a salt is completely ionized, it is a simple matter to calculate the value of $K_{s.p.}$ from the solubility or vice versa. A salt yielding two univalent ions will have a solubility S, equal

[1] As already implied, the compound BA in the solid form is comprised of B^+ and A^- ions arranged in a definite pattern, but to avoid confusion in discussing the solid-solution equilibrium the solid state may be designated as BA.

[2] Strictly speaking, the activities of the ions should be used instead of the concentrations. See p. 105 for a brief discussion of the activity concept.

to the concentration of either ion; for example, in the case of silver chloride,

$$S = [AgCl] = [Ag^+] = [Cl^-]$$

where the concentrations are expressed in moles per liter. If the solubility of silver chloride is measured and at a certain temperature is found to be about 0.0014 g. per liter, then it has dissolved to the extent of $0.0014/143.3 = 10^{-5}$ moles per liter. Since one molecule gives one each of the ions, the complete dissociation of the salt will establish a value of 10^{-5} for both $[Ag^+]$ and $[Cl^-]$ so that

$$K_{s.p.} = [Ag^+][Cl^-] = [10^{-5}]^2 = 10^{-10}$$

Conversely, knowing the value of $K_{s.p.}$ to be 10^{-10}, the solubility would be calculated thus:

$$S = \sqrt{10^{-10}} = 10^{-5} \text{ moles per liter, or}$$
$$S = (10^{-5})(143.3) \cong 0.0014 \text{ g. per liter}$$

The solubility of a salt of the B_2A type, like Ag_2CrO_4, usually is taken as equal to the concentration of the bivalent ion, since each molecule upon ionizing yields one bivalent ion whereas it gives two of the univalent ions. Therefore it follows that the value of $[B^+]$ must be twice that of $[A^-]$, and if we let $[A^-] = X$ then equation (4) becomes

$$(2X)^2 (X) = K_{s.p.}$$

or

$$4X^3 = K_{s.p.} \tag{5}$$

from which, if $K_{s.p.}$ is known, the solubility is calculable. To illustrate: $K_{s.p.}$ for silver chromate has a value of 2.0×10^{-12}. Therefore

$$4X^3 = 2.0 \times 10^{-12}$$
$$X = \sqrt[3]{\frac{2.0 \times 10^{-12}}{4}} = 7.9 \times 10^{-5}$$

The solubility of silver chromate thus is 7.9×10^{-5} moles per liter, or $(7.9 \times 10^{-5})(332) = 0.026$ g. per liter for the temperature taken.

Because the solubility product is based upon equilibrium conditions between solute and solution—that is, a saturated solution—it follows that if the concentrations of the ions of a given salt are such that their product (raised to the proper exponential power) exceeds the value of $K_{s.p.}$, precipitation of the salt must take place until the ion product is decreased to the $K_{s.p.}$ value. If the ion product gives a value less than that of $K_{s.p.}$ the solution will be unsaturated, while a solution containing the ions in such concentrations that their product just equals the value

of $K_{s.p.}$ must be a saturated solution. Thus in a gravimetric analysis the precipitating reagent must be added to the solution of the sample until $K_{s.p.}$ of the precipitate is exceeded, and obviously the $K_{s.p.}$ is most readily exceeded if its value is very small; this is only another way of saying that the analysis should be based upon the precipitation of a so-called "insoluble" salt of the constituent being determined. It also emphasizes the importance of basing the determination upon an irreversible chemical reaction, for it will be recalled that a reaction is complete if an insoluble product is formed. Nothing, of course, is absolutely insoluble, but the less the solubility (the smaller the $K_{s.p.}$) the better the chances for a good quantitative separation of the desired constituent.

It should be pointed out that the relative solubilities of salts are not to be judged directly from their $K_{s.p.}$ values unless they are of the same valence types. For example, silver chloride and silver chromate at room temperature are soluble to the extent of about 0.0015 g. and 0.026 g. per liter respectively. Therefore the $K_{s.p.}$ of silver chloride is

$$\text{AgCl, } K_{s.p.} = \left(\frac{0.0015}{143.3}\right)^2 = 1.1 \times 10^{-10}$$

and that of silver chromate is

$$\text{Ag}_2\text{CrO}_4\text{, } K_{s.p.} = \left(\frac{2 \times 0.026}{332}\right)^2 \left(\frac{0.026}{332}\right) = 4\left(\frac{0.026}{332}\right)^3 = 2.0 \times 10^{-12}$$

Thus, although silver chloride has the lesser solubility, it has the greater solubility product. The reason obviously is that the solubilities of both salts is a fraction of a mole per liter and the cubing of the fraction in the one case gives a smaller value for $K_{s.p.}$ than does the squaring of the fraction in the other case. (In addition, the larger value of the molecular weight of silver chromate contributes somewhat to its smaller solubility product constant.)

Solubility of Salts

Common Ion Effect. The product of the ion concentrations in a saturated solution is limited by the solubility product. Thus if to a saturated solution of silver chloride an excess of silver ion is added the solubility product is momentarily exceeded, and silver chloride must be precipitated until the product of the ion concentrations is sufficiently diminished to reëstablish the $K_{s.p.}$ value. The addition of any compound having an ion in common with either ion of the difficultly soluble solute will decrease the solubility of the latter, that is to say, will cause a more nearly complete precipitation of the latter. This is the well-known common ion effect. Because of this effect it is a rule when precipitating a salt to add a slight excess of the precipitating reagent, since this will always give an excess of a common ion. The amount by which the solubility is decreased

may be illustrated with a saturated silver chloride solution to which excess silver nitrate is added. Since $[Ag^+][Cl^-] = K_{s.p.}$,

$$[Cl^-] = \frac{K_{s.p.}}{[Ag^+]}$$

If silver nitrate is added until the solution is 0.01 M with respect to Ag^+ ion, we have

$$[Cl^-] \cong \frac{10^{-10}}{10^{-2}} = 10^{-8}$$

and since the solubility of silver chloride is identical with the concentration of the Cl^- ion its solubility has been reduced from 10^{-5} to 10^{-8} or a thousandfold. This was to be expected since the silver ion concentration was increased a thousandfold. The same result would be obtained if we added potassium chloride to a saturated solution of silver chloride until the solution was 0.01M with respect to Cl^- ion, for then

$$[Ag^+] \cong \frac{10^{-10}}{10^{-2}} = 10^{-8}$$

The above illustration brings us to another generalization regarding solubility of a salt, namely, that the solubility is measured by the concentration of the ion which is not in excess. If there are 100 chloride ions and 1000 silver ions in a solution we must regard the solution as containing only 100AgCl. Similarly a solution containing 100 silver ions and 1000 chloride ions also must be thought of as containing only 100AgCl. The same reasoning of course applies when the units for expressing the quantities are moles per liter, i.e., the concentrations.

The common ion effect is somewhat different for a salt of a different valence type, e.g., B_2A. If a saturated solution of silver chromate is made 0.01 M with respect to Ag^+ ion, the solubility of the salt is decreased to a greater extent than if the solution were made 0.01 M with respect to the $CrO_4^=$ ion (see Fig. 32). In the first case

$$[CrO_4^=] = \frac{K_{sp}}{[Ag^+]^2}$$

and

$$S_{Ag_2CrO_4} = [CrO_4^=] = \frac{2.0 \times 10^{-12}}{10^{-4}} = 2.0 \times 10^{-8} \text{ moles per liter}$$

but in the latter case

$$[Ag^+]^2 = \frac{K_{s.p.}}{[CrO_4^=]}$$

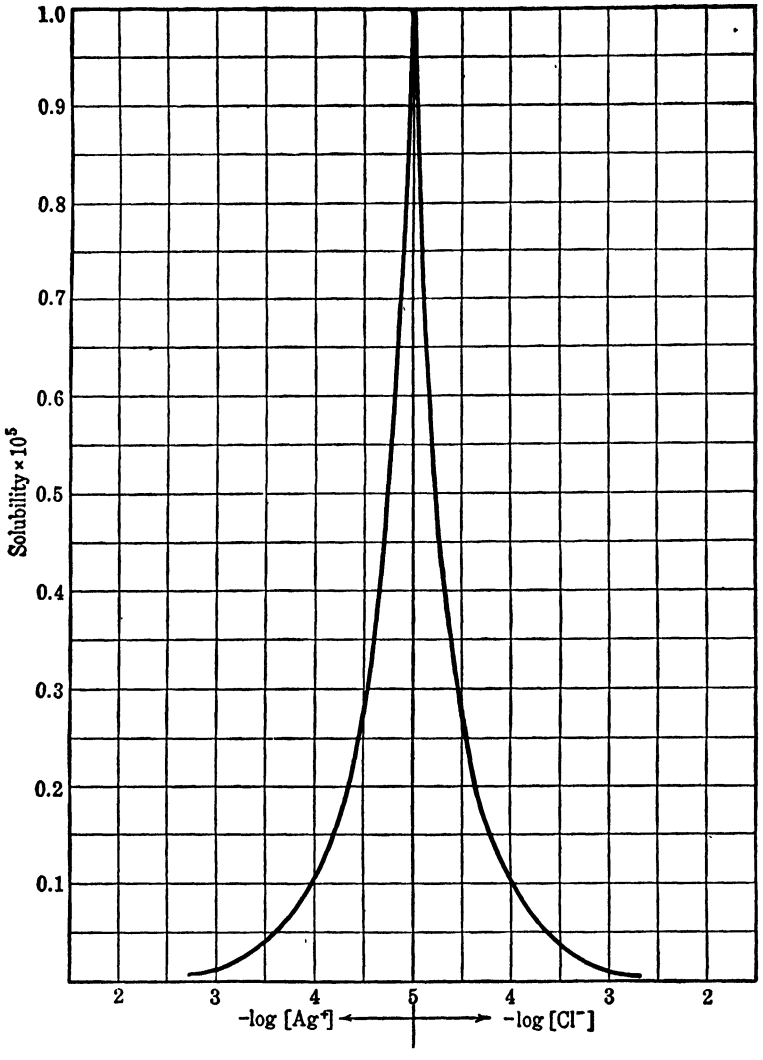


FIG. 31. Solubility of silver chloride in the presence of excess common ion. (From Kolthoff and Sandell: *Quantitative Inorganic Analysis.* By permission of The Macmillan Company, publishers.)

and $$S_{Ag_2CrO_4} = \frac{[Ag^+]}{2} = 0.5\sqrt{\frac{K_{s.p.}}{[CrO_4^{=}]}}$$

$$= 0.5\sqrt{\frac{(2.0 \times 10^{-12})}{10^{-2}}} = 7.1 \times 10^{-6}$$

The common ion effect with various excess concentrations of each ion is shown graphically in Figs. 31 and 32 for silver chloride and for silver

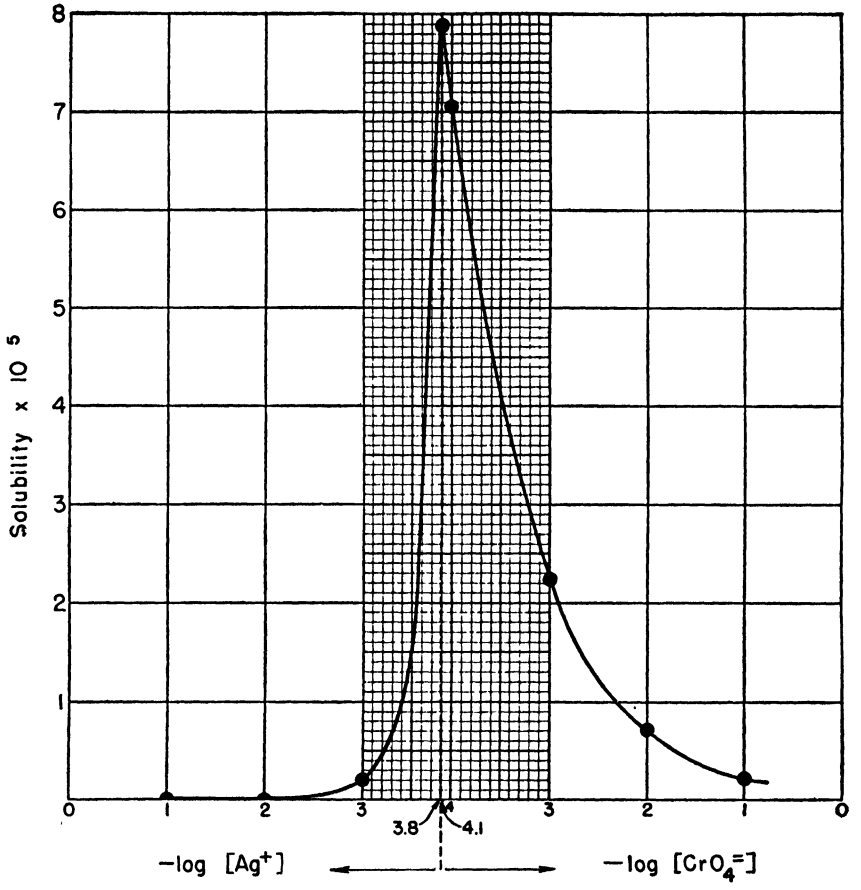


FIG. 32. Solubility of silver chromate in the presence of excess common ion.

chromate. The data for the latter figure are given in Table 18; those for Fig. 31 the student should calculate for himself. Note the symmetrical nature of the silver chloride curve and the asymmetry of the silver chromate curve.[3] In both instances, of course, the cusp of the curve occurs when neither the positive nor the negative ion is in excess; i.e., the solubility of a salt is at a maximum when there is no common ion effect.

Solubility in Solutions Without Common Ion Effect. The Salt Effect. One might be inclined to say, judging from the usual common ion

[3] Fig. 32 is really two graphs joined together. On the left we have the change of solubility of silver chromate with varying excess concentrations of Ag^+ ion; on the right we have the change of solubility with excess concentrations of CrO_4^- ion. When neither ion is in excess, the pAg^+ and $pCrO_4^-$ values must be 3.80 and 4.10; therefore the abscissas of the two adjoining graphs must show 3.80 on the one side coinciding with 4.10 on the other.

Table 18

SOLUBILITY OF Ag_2CrO_4 IN PRESENCE OF EXCESS Ag^+ ION AND EXCESS CrO_4^- ION

$[CrO_4^-]$		$pCrO_4^-$	$[Ag^+]$	pAg^+	*Solubility*
					with CrO_4^- in excess, $S_{Ag_2CrO_4} = 0.5[Ag^+]$
Excess CrO_4^-	10^{-1}	1	4.47×10^{-6}	5.35	$0\ 22 \times 10^{-5}$
	10^{-2}	2	$1\ 41 \times 10^{-5}$	4.85	$0\ 71 \times 10^{-5}$
	10^{-3}	3	$4\ 47 \times 10^{-5}$	4.35	$2\ 24 \times 10^{-5}$
	10^{-4}	4	1.41×10^{-4}	3.85	$7\ 05 \times 10^{-5}$
No excess 7.9×10^{-5}		4.10	1.58×10^{-4}	3 80	$7\ 9 \times 10^{-5}$
					with Ag^+ in excess, $S_{Ag_2CrO_4} = [CrO_4^-]$
Excess Ag^+	2×10^{-6}	5 70	10^{-3}	3	$2\ 0 \times 10^{-6}$
	2×10^{-8}	7 70	10^{-2}	2	$2\ 0 \times 10^{-8}$
	2×10^{-10}	9.70	10^{-1}	1	$2\ 0 \times 10^{-10}$

effect, that in gravimetric analysis it would be a good idea to add a large excess of precipitating reagent inasmuch as the common ion effect thereby would become more pronounced. However, as may be seen in Figs. 31 and 32, a small excess of common ion is almost as effective as a large excess. Furthermore, as a rule, a difficultly soluble salt dissolves to a greater extent in a solution containing a moderate or a high concentration of an electrolyte than it does in water alone, whether or not a common ion effect is at play. In almost all of our applications of the Law of Mass Action it is possible to employ the concentrations of the ions involved instead of the active masses. This usually introduces no serious error. Occasionally, though, it is necessary to avoid this approximation if we are to understand certain unusual effects. It has already been pointed out that the active mass is represented by the activity and not the concentration. The activity, a, and the concentration, c, are related thus:

$$a = fc \tag{6}$$

where f is the activity coefficient mentioned in Chapter 7, p. 105. As a given solution becomes more dilute, f approaches unity, so that at infinite dilution a and c become equal. The value of a for an ion in moderately concentrated solutions depends upon the valence and upon what other ions are present in the solution, for interionic attraction will vary as these conditions change. If we employ activities instead of concentrations for the difficultly soluble salt, BA, we have

$$a\mathrm{B}^+ . a\mathrm{A}^- = \mathrm{S}_{\mathrm{BA}} \tag{7}$$

where aB^+ and aA^- represent the activities of the two ions and S represents the thermodynamic solubility product. Combining equations (6) and (7)

$$[B^+][A^-]f_{B^+}.f_{A^-} = S_{BA} \tag{8}$$

or

$$[B^+][A^-] = \frac{S_{BA}}{f_{B^+} \cdot f_{A^-}} \tag{9}$$

In a saturated solution of a salt only very slightly soluble in water, the dilution is great and the values of f_{B^+} and f_{A^-} are almost unity; thus the thermodynamic solubility product becomes sensibly equal to the classical solubility product. However, in the presence of other electrolytes f_{B^+} and f_{A^-} decrease in value so that, in order that S_{BA} of equation (8) may remain constant, the values of $[B^+]$ and $[A^-]$ must increase; that is to say, the solubility of the difficultly soluble salt, BA, increases in a solution of an electrolyte beyond what it is in a pure water solution. This is known as the salt effect.

Lewis and Randall[4] have shown how the solubility product of a salt in the presence of foreign ions may be obtained. Although the solubility product of calcium sulfate, for example, is quite different when measured in the presence of different *concentrations* of foreign salts (see Fig. 33), there is a remarkable consistency revealed if the solubility product is studied with variations in the ionic strengths, μ, of the foreign salts. The ionic strength is defined as half of the sum of the products of the concentration and the square of the valence of each ion present, or

$$\mu = 0.5\Sigma(MZ^2) \tag{10}$$

where Σ is the summation symbol, M the molarity[5] and Z the valence. (For example, if the salt XY dissolves to the extent of 0.02 mole per liter in a 0 01 M solution of B_2A, the value of μ is half the sum of (0.02) $(1)^2$ for X^+, (0.02) $(1)^2$ for Y^-, (0.02) $(1)^2$ for B^+ and (0.01) $(2)^2$ for A^-; hence = 0.050.) If, now, the solubility product of calcium sulfate is plotted against ionic strength, as in Fig. 34, it is evident that in fairly dilute solutions the solubility product is proportional to the ionic strength no matter what the foreign salt be (contrast Fig. 33). Even at greater ionic strength the variation of the solubility product is small; for example, when $\mu = 0.1$ it is seen that the solubility product of calcium sulfate in the three different solutions is 10^{-4} times 3.4, 3.4 and 3.5. The particular value of the concept of ionic strength is that in dilute solutions the

[4] Lewis and Randall, *Thermodynamics*, The McGraw-Hill Book Co., New York, 1923, pp. 373–383.

[5] Strictly speaking, the molality.

activity coefficient of a strong electrolyte is the same in all solutions of the same ionic strength.

It should be noted that the salt effect manifests itself even when one of the ions of the foreign salt is common with one of those coming from the difficultly soluble salt. In such a case we have two opposing forces in operation. When the excess of the common ion is not great, the result

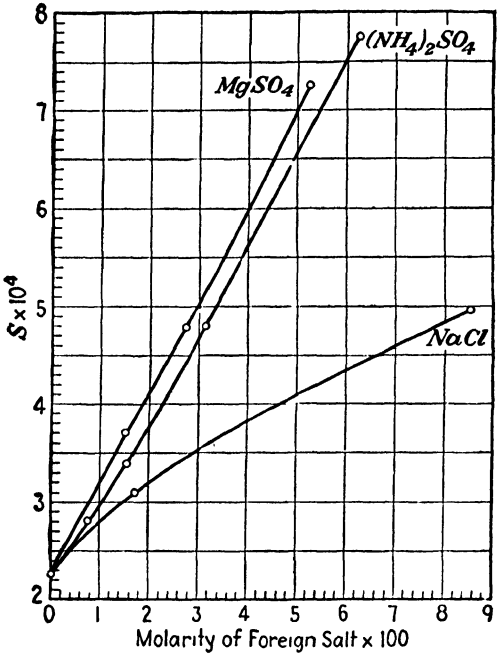


FIG. 33. Change in the value of $K_{sp.}$ for calcium sulfate with change in molarity of foreign salts. (Courtesy, Rieman, Neuss and Naiman: *Quantitative Analysis*, New York, McGraw-Hill Book Co.)

will be the usual common ion effect and the slight excess causes a more nearly complete precipitation of the difficultly soluble salt. But if the excess ion is added to an extent much greater than 0.01 *M*, the salt effect begins, as a rule, to predominate, and the solubility of the salt we wish to precipitate is increased. Accordingly, one should avoid the addition of a large excess of precipitating reagent in quantitative separations.

Complex Ions and Solubility. Sometimes it happens that the ions of a precipitate will react with an excess of the precipitating reagent to form a stable complex ion. Again, an ion from the precipitate may react with another ion not common with either ion of the precipitated substance. In either case the formation of the complex ion must deplete,

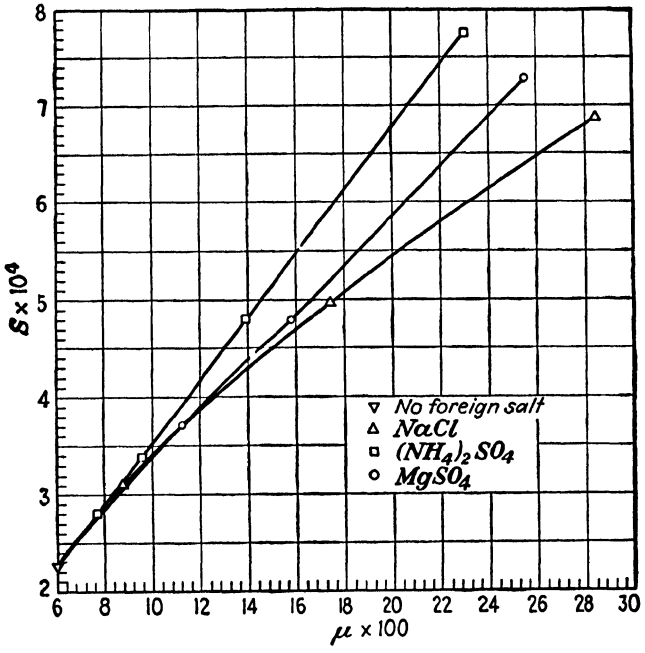


FIG. 34. Change in the value of $K_{s.p.}$ for calcium sulfate with change in the ionic strength. (Courtesy, Rieman, Neuss and Naiman: *Quantitative Analysis*, New York, McGraw-Hill Book Co.)

though not exhaust, one of the ions coming from the precipitate, and this would tend to lower the ion product for the difficultly soluble compound. Therefore, further solution of the compound must result to establish again its characteristic solubility product. Thus when a complex ion is formed by the addition of excess precipitating reagent, instead of the common ion reducing the solubility, an increased solution takes place. The addition of excess ammonia to copper, nickel and silver salts, or of sodium hydroxide to lead and aluminum salts, illustrates this type of reaction. Such reactions often provide means of bringing about separations in analytical chemistry; this has already been encountered in qualitative analysis. The quantitative treatment of complex ion formation may be illustrated with the silver and cyanide ions. If some solid silver argenticyanide is placed in pure water (or if a soluble cyanide and a soluble silver salt are brought together in solution and silver argenticyanide is precipitated), two equilibria are set up:

$$\underset{\text{(solid)}}{Ag[Ag(CN)_2]} \rightleftarrows Ag^+ + Ag(CN)_2^-, \text{ whence}$$

$$[Ag^+][Ag(CN)_2^-] = K_1 \tag{11}$$

and

$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2(CN)^-, \text{ from which}$$

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = K_2 \tag{12}$$

K_1 and K_2 have been determined as 2.2×10^{-12} and 1.0×10^{-21} respectively. What now will be the effect of adding excess cyanide ion to the solution where both of these equilibria prevail?

First it is necessary to show that practically all of the silver ion in the solution comes from the first of the above dissociations. Obviously from equation (11) the silver ion concentration, and that of the argenticyanide ion as well, is $\sqrt{2.2 \times 10^{-12}} = 1.5 \times 10^{-6}$. The silver ion concentration coming from the second of the two dissociations may be calculated, since we know that if we let the value of $[Ag^+]$ from this source be X, then $[CN^-] = 2X$, and $[Ag(CN)_2^-]$, we have already seen, is 1.5×10^{-6}. Therefore

$$\frac{(X)(2X)^2}{1.5 \times 10^{-6}} = 1.0 \times 10^{-21}$$

from which X or $[Ag^+] = 7.2 \times 10^{-10}$. Thus practically all of the silver ion comes from the first equilibrium; the total value of $[Ag^+] \cong 1.5 \times 10^{-6}$.

Suppose that enough potassium cyanide is added to the solution to reduce the silver ion concentration (by shifting the equilibrium, $Ag(CN)_2^- \rightleftarrows Ag^+ + 2(CN)^-$, to the left) from 1.5×10^{-6} to 1.0×10^{-6}. This eliminates a concentration of silver ion amounting to 0.5×10^{-6} and causes an equal increase of argenticyanide ion concentration. Momentarily, then, the ion product, equation (11), will be

$$[1.0 \times 10^{-6}][(1.5 \times 10^{-6}) + (0.5 \times 10^{-6})] = 2.0 \times 10^{-12}$$

which is less than the solubility product for these ions—namely, 2.2×10^{-12}—so that the precipitate must proceed to dissolve until the $K_{s.p.}$ value is reëstablished. Thus, because of complex ion formation, we have the reverse of the usual common ion effect. (What would be the effect of adding excess silver nitrate to a precipitate of silver argenticyanide?)

Hydrogen Ion Concentration and Solubility of Salts. Difficultly soluble salts of strong acids are neither more nor less soluble in strong acid solutions than they are in salt solutions of comparable ionic strength. But a difficultly soluble salt of a weak acid will dissolve if treated with a strong acid. Consider calcium oxalate. The small amount which dissolves in water dissociates completely:

$$\underset{\text{(solid)}}{CaC_2O_4} \rightleftarrows Ca^+ + C_2O_4^-$$

If a strong acid is added to a precipitate of calcium oxalate the hydrogen ions will combine with oxalate ions, since oxalic acid is a weak acid and because the ionization of the oxalic acid which is formed is repressed by the excess hydrogen ion from the strong acid. The result is that the value of $[C_2O_4^{=}]$ is reduced to such a point that the ion product of $[Ca^{++}][C_2O_4^{=}]$ falls below $K_{s.p.}$ for calcium oxalate; therefore the solid salt must dissolve in its attempt to restore $K_{s.p.}$ to its constant value. The newly formed oxalate ion now combines with hydrogen ion, provided enough of the strong acid was added, thus allowing for a continuation of the dissolving process until, finally, all of the calcium oxalate may be dissolved. Obviously, for solution to take place it is necessary that the value of the anion concentration, after adding the strong acid, be less than that which the salt itself would establish in the absence of acid. The higher the value of $K_{s.p.}$ for the salt and the smaller the value of K_a for the weak acid which is formed, the easier may this be accomplished. Quantitative procedures often take advantage of the solvent effect of acids, varying as it must with the two factors just mentioned. The precipitation of silver chloride, in the gravimetric determination of chloride or of silver, is carried out in a slightly acidic solution. This prevents the simultaneous precipitation of other anions, since silver salts, arsenates, carbonates, chromates, oxalates, etc., are soluble in slightly acidified solutions. The quantitative precipitation of salts which dissolve in acidic solutions must, of course, be carried out in a basic solution. Indeed, it may be said that in almost every instance where the principle of solubility product is involved the hydrogen ion concentration is a matter of utmost importance.

Fractional Precipitation. Separation of Ions Which Are Precipitated by the Same Reagent. Usually the precipitation of a certain ion in the form of one of its slightly soluble compounds takes place in a solution containing several ions other than the one which it is desired to determine. In other words, the purpose is to precipitate a single substance in a solution containing, as a rule, several ions of like charge; thus the term, fractional precipitation. In only a minority of cases is it true, when the precipitating reagent is added to a solution containing many ions of like sign, that the solubility product principle rigorously governs the precipitation which occurs. There are a few, however, and as an illustration we may consider the precipitation of silver chloride from a solution containing both chloride ions and chromate ions. Here, both anions behave independently; that is, neither is precipitated upon the addition of silver ion until the product of the concentration of the anion times that of the silver ion raised to the proper power exceeds the $K_{s.p.}$ value of the compound. This fact is the basis of the Mohr method for the volumetric determination of chlorides which is described elsewhere in this text (see p. 283).

The solubility products of silver chloride and silver chromate are roughly,

$$[Ag^+][Cl^-] = 1 \times 10^{-10}$$
$$[Ag^+]^2[CrO_4^-] = 2 \times 10^{-12}$$

If silver nitrate solution is added to a solution containing both chloride ion and chromate ion, each of the above conditions must be satisfied at the same time. If we square the equation for silver chloride and divide by that for silver chromate, the silver ion cancels out and we obtain

$$\frac{[Cl^-]^2}{[CrO_4^-]} = \frac{1}{2 \times 10^8} \tag{13}$$

This is to say that when both silver chloride and silver chromate are in equilibrium with the supernatant liquid the concentration of the chloride ion when squared will be one two hundred millionth of the concentration of the chromate ion. Obviously the concentration of chloride ion which may remain in solution with chromate ion when the two are at equilibrium with silver ion may be only very small; practically speaking, zero.

If, therefore, silver ion is added, say to equivalent quantities of chloride and chromate ions in the same solution, silver chloride will precipitate alone until the chloride ion is so reduced in concentration that the conditions of equation (13) are realized. After this both silver chloride and silver chromate will precipitate, and in this same ratio, since the statement embodied in equation (13) may be maintained in the supernatant liquid only if, once both begin to precipitate, they do so in this ratio.

Evidently in order that one substance be practically completely precipitated before the other begins to form it is necessary that the solubility products of the two substances be considerably different in magnitude. Another example is a mixture of iodide and chloride which when dissolved may be separated by the addition of silver ion, since $K_{s.p.}$ for silver iodide is 10^{-16} while that for silver chloride, as already mentioned, is 10^{-10}. The student should calculate the relative amounts of chloride and iodide in solution after both precipitates are in equilibrium with the solution.

Fractional Precipitation Regulated by Controlled pH. A discussion of buffer action is given in Chapter 7, p. 97. The means described there for obtaining and maintaining a definite hydrogen ion concentration must be kept in mind in considering the following aspects of fractional precipitation.

We recall from qualitative analysis the importance of carefully controlling the pH of the solution in the separation of the copper-arsenic group of metals as sulfides from the metallic ions of subsequent groups. A saturated solution of hydrogen sulfide at room temperature is approxi-

mately 0.1 *M*. If the hydrogen ion concentration is adjusted to about 0.3 *M* we have

$$\frac{[H^+]^2[S^=]}{[H_2S]} = \frac{(0.3)^2[S^=]}{0.1} = 1.1 \times 10^{-22}$$

or

$$[S^=] = 1.2 \times 10^{-22} \tag{14}$$

Now the solubility product of copper sulfide is about 10^{-45} and that of zinc sulfide is about 10^{-23}. Thus, if precipitation of copper sulfide is to be avoided when one of its salts is treated with a solution saturated with hydrogen sulfide and 0.3 *M* with respect to hydrogen ion, the concentration of copper ion must be equal to or less than 10^{-23}, i.e.,

$$[Cu^{++}] \leqq \frac{10^{-45}}{10^{-22}} = 10^{-23}$$

whereas the similar calculation for zinc ion yields

$$[Zn^{++}] \leqq \frac{10^{-23}}{10^{-22}} = 10^{-1}$$

This means that with the hydrogen ion concentration so controlled (and, therefore, also the sulfide ion concentration) only about 6.4×10^{-22} g. per liter of copper, but 6.5 g. per liter of zinc, could remain in solution. In other words, it would be difficult to prevent practically all of the copper from being precipitated, but any amount of zinc up to 0.1 mole, or 6.5 g., per liter would remain dissolved after treating with the hydrogen sulfide. A different value for hydrogen ion concentration would establish a different sulfide ion concentration, for the latter obviously varies inversely as the square of the former; accordingly, carelessness in regulating the acidity in sulfide separations may easily result in the precipitation of sulfides of iron, aluminum, etc., if these ions are present.

Likewise a strict control of hydrogen ion concentration is necessary if ferric hydroxide is to be precipitated alone in the presence of magnesium ions. The solubility products for ferric hydroxide and magnesium hydroxide are 1.1×10^{-36} and 1.2×10^{-11}. If to a solution containing both ferric ions and magnesium ions a properly buffered solution of ammonium hydroxide is added, ferric hydroxide may be precipitated without throwing out any magnesium hydroxide. Suppose we have a solution which is 0.05 *M* with respect to both Fe^{+++} and Mg^{++} and to it is added sufficient ammonium hydroxide and ammonium chloride to make the solution 0.1 *M* in regard to each. The question is: What will precipitate, if anything?

The answer is simple once we know the value of $[OH^-]$. This may be

calculated from the dissociation constant of the base, namely, 1.8×10^{-5}, and the concentration of the salt.[6]

If

$$X = [OH^-]$$

then

$$0.1 + X = [NH_4^+]$$

and

$$0.1 - X = [NH_4OH]$$

Substituting the above in the mass law expression,

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}, \text{ we obtain}$$

$$\frac{(0.1 + X)(X)}{(0.1 - X)} = 1.8 \times 10^{-5} \text{ or}$$

$$[OH^-] = X = 1.8 \times 10^{-5}$$

Therefore the ion product for ferric ion and hydroxyl ion in the solubility product expression is

$$(5 \times 10^{-2})(1.8 \times 10^{-5})^3 = 2.9 \times 10^{-16}$$

which is greater than $K_{sp.}$ for ferric hydroxide, and therefore it precipitates. At the same time the ion product for magnesium ion and hydroxyl ion in the solubility product expression is

$$(5 \times 10^{-2})(1.8 \times 10^{-5})^2 = 1.6 \times 10^{-11}$$

which is almost equal to the $K_{sp.}$ for $Mg(OH)_2$. The fact that the ion product is very slightly higher than the K_{sp} does not mean that precipitation of magnesium hydroxide will certainly occur, since, due to the tendency to form supersaturated solutions, it is necessary as a rule that the ion product exceed the $K_{sp.}$ to a considerable extent. However, theoretically it would be necessary to use somewhat more ammonium chloride than was stated in the above problem, thus further repressing the ionization of the ammonium hydroxide, to be certain that no magnesium hydroxide would precipitate. The student should calculate exactly what is the smallest possible concentration of the salt which

[6] The $[OH^-]$, of course, may be computed from the buffer equation of Chapter 7, p. 98. That is,

$$[OH^-] = \frac{[BOH]}{C} \cdot K_b$$

$$= \frac{0.1}{0.1}(1.8 \times 10^{-5})$$

$$[OH^-] = 1.8 \times 10^{-5}$$

would make the precipitation of magnesium hydroxide impossible. (*Answer:* 0.12 *M.*)

Questions

(See also p. 246)

1. Explain under what circumstances the relative solubilities of salts in grams per liter may or may not be judged directly from their $K_{sp.}$ values.
2. The common ion effect upon the solubility of a salt may be shown graphically by plotting the solubility against the negative logarithm of the excess ion as in Figs. 31 and 32. What types of salts will yield symmetrical curves?
3. Why does f, the activity coefficient, approach unity as the dilution becomes very great?
4. Explain how the solubility of a precipitate is rendered greater (a) if one of its ions reacts to form a complex ion, or (b) through the salt effect (see p. 227).

Chapter 14

COPRECIPITATION

In GRAVIMETRIC analyses when a substance is precipitated, washed, dried and weighed the percentage of the essential constituent present in the original sample may be calculated if, and only if, the precipitate consists entirely of a compound of definite and known composition. In accordance with the solubility product principle the analyst avoids exceeding the $K_{s.p.}$ of all compounds except that which he wishes to precipitate. However, it is unfortunately a fact that very often during a precipitation not only the desired substance is thrown out of solution, but, in addition, quantities, usually small but significant, of other substances the solubility products of which have not been exceeded. This phenomenon is known as coprecipitation, and the contamination of precipitates resulting from coprecipitation is one of the most common causes of inaccurate analyses. Some compounds, such as silver chloride, separate in a fairly pure form, but many others, barium sulfate for example, do not do so under ordinary conditions. It is by no means always a fact that the contaminating substance is one which itself is a difficultly soluble substance. It is true that when copper sulfide is precipitated from a solution also containing zinc ions a small amount of zinc sulfide is carried down, and that when ferric hydroxide is precipitated with ammonia from a solution also containing cupric ion some copper hydroxide is found to contaminate the precipitate. But highly soluble substances also are coprecipitated in many instances. For example, barium sulfate, given the chance, will drag down with it ferric sulfate or barium nitrate, to mention only two, both of which are quite soluble. The study of coprecipitation would be comparatively simple if there were a consistent pattern of behavior always exhibited when a precipitate shows an unexpected impurity. The fact is, however, that while a few signs of conformity of behavior have been observed, to a large extent each is a case to itself, so that it is at present difficult to make predictions or set forth rules which would enable us, in advance of actual experimentation, to say whether or not contamination of a certain precipitate is likely to occur under a given set of conditions. Nevertheless, from the considerable amount of data which has been accumulated on the subject, we often are able to say what appear to be causative factors, and to confine the contamination within reasonable bounds, if not prevent it. When this

is not possible an attempt may be made to arrange conditions so that unavoidable positive or negative errors of coprecipitation are compensated by intentional and nullifying negative or positive errors of about the same magnitude. The precipitation of barium sulfate is an example of such a compensation.[1]

The Colloidal State. Examples have already been encountered in qualitative analysis when precipitates were obtained in such a finely divided state that the particles passed through the filter. Often the oxidation of hydrogen sulfide causes a precipitate of sulfur comprised of such fine particles that they will not settle in a reasonable length of time and cannot be filtered out of the solution. Such particles are known as a temporary suspension; they are recognizable as a separate phase. The diameter of such particles is about 10^{-5} cm. Each consists of many molecules, or atoms, since the diameter of a single molecule is around 10^{-7} or 10^{-8} cm. Under the effect of gravity the particles of a suspension eventually would settle. But if the particles happen to assume a size somewhat smaller than 10^{-5} cm. a condition of affairs results which is quite different from that prevailing in a suspension. No separate phase can be seen (there is no cloudiness in the solution); however, a path of light through the liquid becomes visible when viewed transversely (Tyndall effect). Furthermore, a separation of these *colloidal* particles from the solution can be accomplished through *dialysis*, that is, by the use of a semipermeable membrane which will allow the passage of the molecules of a true solution but will retain the colloidal particles. Thus a colloidal dispersion may be defined as a system in which the particles of the dispersed phase are intermediate in size between those of a suspension and a true solution, the latter being characterized by a subdivision of the solute down to molecular or ionic magnitudes.

It is not surprising that a colloidal dispersion should be quite different in properties from both true solutions and suspensions. A true solution is homogeneous, if not philosophically, at least practically speaking; a colloidal dispersion is heterogeneous, for there are two phases: the dispersed phase and the dispersing medium. A suspension, given time enough, will settle out from the solution, thus revealing its heterogeneity. A solution exhibits colligative properties which depend upon the number of particles: osmotic pressure, increase of boiling point, decrease of freezing point and lowering of vapor pressure. Colloidal dispersions do not exhibit these properties.

In analytical chemistry we are usually concerned only with colloidal dispersions in which the dispersion medium is water. Such dispersions are called *hydrosols*. They may be roughly grouped into two classes, *hydrophobic* colloids, or those in which the particles do not show a

[1] Fales and Thompson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 206 (1939).

strong affinity for the dispersion medium, water; and *hydrophilic* colloids, or those whose particles do exhibit a strong affinity for water. Upon coagulation the former retain relatively little water, while the latter coagulate to yield gelatinous solids which carry a large amount of water; in the coagulated form they are known as *gels*.

For the most part the hydrosols met in analytical chemistry are electrically charged, either positively or negatively, due to the fact that they adsorb either cations or anions from the solution in which the particles are dispersed. Arsenious sulfide, for example, may be prepared as a colloidal dispersion; the particles assume a negative charge by adsorbing sulfide ions on their surfaces. Ferric hydroxide, as a colloidal dispersion, takes on a positive charge. When colloidal dispersions are electrolyzed they lose their electrical charge and become coagulated. They also are coagulated by the addition of an electrolyte which will furnish ions to serve as centers of attraction around which the colloidal particles may cluster and thus flocculate. It is the reverse of this process—that is, the removal of the ions which serve to flocculate the colloidal particles—which accounts for the annoying experience of leakage through the filter when a coagulated precipitate is washed free of foreign ions. The precipitate, in part, simply reverts to a colloidal dispersion. Such *peptization* can be prevented by washing, not with pure water, but with a solution of an electrolyte which later, usually during the ignition of the precipitate, may be removed.

Both hydrophobic and hydrophilic colloidal dispersions are met in quantitative work. They are troublesome not only because they cannot be filtered but also because, due to the large aggregate surface area which such small particles must possess, they tend to attach relatively large amounts of foreign ions to these surfaces. Even though coagulated they retain much of the contaminating substances. It therefore is necessary to control conditions so that precipitation is effected without any concomitant formation of a colloidal state. When the solubility product of a salt in a true solution is exceeded a supersaturated solution results. Precipitation follows supersaturation and the crystallization of the substance occurs about centers of nucleation within the solution. The development of these centers depends chiefly upon the temperature and the presence of foreign bodies. If the rate of nucleation is low while the rate of crystal growth is high, the result will be the precipitation of fewer and larger particles. A high rate of nucleation and a low rate of crystal growth promote many small particles and may even bring about a colloidal dispersion. This of course is undesirable since the presence of a great number of very small particles, whether they actually attain colloidal dimensions or not, means a large surface area which, in turn, leads to adsorption of impurities.

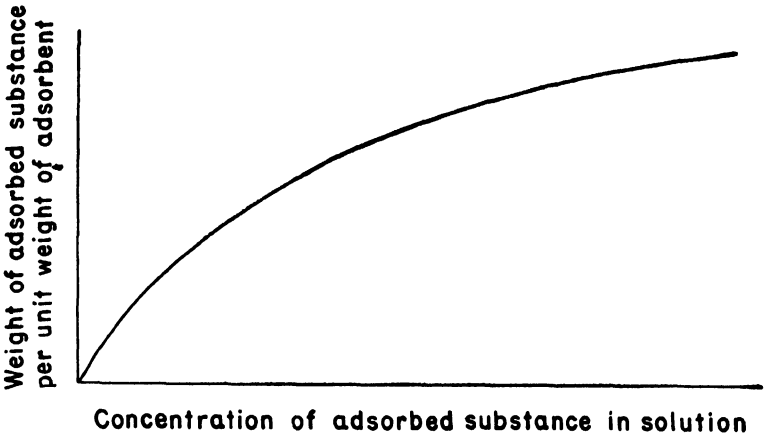


FIG. 35. Coprecipitation as a function of the concentration of the contaminating salt.

Adsorption. Adsorption may be defined as the increase in concentration of a substance, molecule or ion, at the surface of a solid in contact with a solution of those molecules or ions. If an aqueous solution of hydrogen sulfide is shaken with particles of activated charcoal, and the solution is then filtered, it will be found that the odor is hardly noticeable. The molecules of hydrogen sulfide have been attracted to the surface of the charcoal particles and thus removed from the solution; they have been adsorbed. Considerable evidence exists which indicates that adsorption frequently is the reason back of coprecipitation. Let us examine some of this evidence.

Adsorption equilibria in general are found to follow the law formulated by Freundlich,[2]

$$X = kC^{1/n}$$

where X is the weight of substance adsorbed per unit weight of adsorbing solid, C is the concentration of the adsorbed substance in the solution, k and n are constants, the latter usually having a value from 1 to 5. The graph for the above equation yields different curves depending upon the values of the constants but, in general, takes a parabolic form as seen in Fig. 35.

The Freundlich equation indicates that if the coprecipitated substance is adsorbed its quantity should be proportional to its concentration in the supernatant liquid. That is, as the concentration of the objectionable ion becomes greater, the amount coprecipitated will become

[2] Freundlich, *Z. physik. Chem.*, 57, 385 (1907).

greater. There are many experimental confirmations of this. Blasdale[3] precipitated barium sulfate from a series of equimolar solutions of sulfuric acid containing differing amounts of potassium nitrate. With 0.2000 g. of potassium nitrate present the barium sulfate was found to be contaminated with 0.0062 g. of potassium nitrate; with 1.0000 g. of potassium nitrate in the solution the precipitate carried down 0.0182 g. of the nitrate; and with 5.0000 g. of potassium nitrate originally present in the solution 0.0354 g. of it was coprecipitated. If these data are plotted in the manner of Fig. 35 the points fall very well on a curve represented by the equation, $X = kC^{1/2}$; that is to say, the data fit the Freundlich equation. The same kind of evidence for adsorption of the coprecipitated ion is furnished by Lehrman, Been and Manes[4] in their studies of the coprecipitation of barium ion by aluminum, chromium and ferric hydroxides.

It appears that coprecipitation usually takes place, at least with crystalline precipitates, simultaneously with the precipitation. In other experiments by Blasdale 1.0000 g. of potassium nitrate was added to the suspension of barium sulfate *after* it was precipitated and only 0.0024 g. of potassium nitrate was found to contaminate the precipitate. On the other hand Kolthoff and Moskovitz[5] found that cupric ion is adsorbed by gelatinous ferric hydroxide precipitate to the same extent regardless of whether copper chloride is added before or after the precipitation of the ferric hydroxide. Furthermore, these investigators found that the extent of coprecipitation of cupric ion with ferric hydroxide was not altered by digestion of the precipitate even up to 69 hours. This rather strongly suggests that adsorption of the coprecipitated ion is at play, since, unlike the situation when dealing with crystalline precipitates, the digestion of gelatinous precipitates does not greatly change the surface area, and adsorption, being a surface phenomenon, should therefore remain constant.

Another point of interest, and one which indicates the frequency with which coprecipitation is due to adsorption, is the fact that generally those ions which are the worst offenders in coprecipitating with precipitates of large surface area are ions of high valence type. Other things being equal, many hydroxide precipitates will drag down larger amounts of sulfate ion, for example, than nitrate ion. This conforms to the fairly well established fact that crystalline substances generally adsorb greater quantities of multivalent ions.

Much of the evidence mentioned above seems to indicate that ad-

[3] Blasdale, *The Fundamentals of Quantitative Analysis*, D. Van Nostrand Co., New York, 1928, p. 138.

[4] Lehrman, Been and Manes, *J. Am. Chem. Soc.*, **62**, 1014 (1940).

[5] Kolthoff and Moskovitz, *J. Phys. Chem.*, **41**, 629 (1937).

sorption is the principal cause of coprecipitation. However, there are other examples of contamination of a precipitate in which adsorption *per se* is not the primary factor.

Occlusion. Adsorption of an impurity during the growth of a crystal is called occlusion. The contaminant may be adsorbed upon the surface of the small crystals of the desired precipitate as they are being formed, without entering into and becoming a part of the crystal lattice, and as the crystals grow the contaminating ions are entrapped within the crystal. It does sometimes happen that a foreign ion may actually replace an ion of the same sign in the crystal lattice; this leads to the formation of a solid solution. Thus if crystals of calcium oxalate monohydrate are agitated with dilute solutions of potassium sulfate,[6] some of the oxalate ions of the crystal lattice are replaced by sulfate ions; shaken with a dilute solution of barium chloride, some of the calcium ions are replaced by barium ions. The less soluble the compound formed between one of the ions in the lattice of the precipitate and the foreign ion of opposite sign, the greater the likelihood that the latter ion will enter the crystal lattice of the precipitate by replacement. Schneider and Rieman[7] have shown this to be generally true in their study of the coprecipitation of certain anions by barium sulfate. Of the six ions studied they found that the extent of occlusion varied inversely with the solubility of the corresponding barium salt with the exception of nitrite ion. Thus while the solubilities of the barium salts of I^-, Br^-, Cl^-, ClO_3^- and NO_3^- ions decrease in the order named, the extent of coprecipitation of these ions with barium sulfate was exactly in the reverse order. Nitrite ion proved to be an exception, possibly because it fits into the barium sulfate lattice better than the other anions mentioned.

It is clear that in cases where occlusion is known to be the cause of coprecipitation, digestion of the precipitate should decrease the extent of occlusion. This is true because during digestion ions from the surface of the crystals are continuously leaving the solid surfaces while ions from the saturated solution are redepositing. Furthermore, as has been mentioned already (p. 8), digestion brings about fewer and larger crystals. While these changes are taking place foreign ions to some extent are eliminated from the crystals and the contamination of the precipitate therefore is decreased.

It frequently happens in cases where occlusion is known to take place that the *order* in which two reacting solutions are brought together governs the question of what the occluded ion will be. When a solution containing the anion of the precipitate is added slowly to one containing the cation of the precipitate, the occlusion of anions takes place to a much

[6] Kolthoff and Sandell, *J. Am. Chem. Soc.*, 55, 2170 (1933).
[7] Schneider and Rieman, *J. Am. Chem. Soc.*, 59, 354 (1937).

greater extent than does the occlusion of cations. Bringing the reagents together in the reverse order causes the occlusion of excess cations. When sulfate ions are added slowly to a solution of barium chloride the crystals of barium sulfate are formed in an environment containing excess barium ions. Thus a small crystal, immediately after being formed, starts to grow by attaching barium ions which largely will find their counterparts in sulfate ions as soon as more solution containing sulfate is added. If this addition is slow, however, the counterpart to some barium ions of the newly forming row or layer of the lattice will be made up of chloride ions of which there is an abundance. Then as more sulfate ions are added and the crystal of barium sulfate grows larger, some of the chloride ions find themselves trapped and embedded beneath the layer of alternating barium and sulfate ions in the now larger crystal. Thus when the growth of the crystal takes place while the cations (of the precipitate) are in excess in the solution (that is, when the reagent slowly being added contains the anion of the precipitate), anion occlusion predominates.

Schneider and Rieman[7] demonstrated this type of selective occlusion by barium sulfate by pouring a solution of sodium sulfate into a solution of barium chloride and then reversing the process. The amount of chloride ion occluded when the former method was carried out was found to be six times greater than when the latter was employed.

Postprecipitation. As the name implies, this term denotes the contamination of a precipitate by an impurity which comes out of solution *after* the primary precipitation has been effected. Braithwaite and Fales[8] showed that when copper sulfide is precipitated from a solution containing zinc and cupric ions, and the precipitate is digested, the amount of zinc sulfide contaminating the copper sulfide increases with the time of digestion. Another example of postprecipitation is encountered when calcium oxalate is precipitated from a solution containing magnesium ions. As usually carried out in the laboratory in the determination of calcium, sufficient oxalate ion is added to exceed not only the solubility product of calcium oxalate but probably that of magnesium oxalate as well.[9] Nevertheless, only a small amount of magnesium is found in the precipitate. This is because the rate of precipitation of magnesium oxalate is very slow. If, however, the precipitate of calcium oxalate is digested for a day or so, much of the magnesium oxalate will have precipitated. In general, if the amount of the impurity increases with the length of time the precipitate remains in contact with the mother liquor, we obviously are dealing with postprecipitation.

[8] Fales and Kenny, *Inorganic Quantitative Analysis*, D. Appleton-Century Co., New York, 1939, p. 241.

[9] See Pedersen, *Trans. Faraday Soc.*, 35, 276 (1939).

Minimization of Coprecipitation Errors

It is often impossible to prevent errors due to coprecipitation, but it is usually possible to reduce such errors to reasonable limits. Before outlining the means of limiting the extent of coprecipitation it should be pointed out that the error caused by such contamination is not necessarily positive. If an ion of the impurity actually enters the crystal lattice of the desired precipitate, and if that ion—for example, sodium—is lighter than the one it replaces, the resulting error obviously will be negative. If an ammonium salt contaminates a precipitate it will be volatilized during the ignition of the precipitate. Therefore it may cause no error at all if its coprecipitation was simple adsorption, for example; but if the ammonium ion excluded an equivalent quantity of cation of the precipitate then a negative error will result since the weight of the former is so small.

Since the adsorption of impurities follows the Freundlich equation, coprecipitation by adsorption is minimized by keeping the concentration of the salt which is coprecipitated as low as possible. In the first place, if the sample for analysis does not dissolve in water it should be brought into solution without introducing an ion known to cause trouble. For example, if the choice of a solvent were between hydrochloric and nitric acids and if the precipitate is known to adsorb or occlude nitrate ion it would be unwise to use nitric acid to dissolve the sample. When, once in solution, it is not practicable to remove the objectionable substance by such means as evaporation or precipitation, then the solution should be made as dilute as permissible before the precipitating reagent is added. If the precipitating reagent itself is coprecipitated, then it too should be diluted before its addition, and it should be added slowly and with stirring in order to prevent localized regions of high concentration during the precipitation. In some cases the contaminated precipitate is dissolved and reprecipitated. The repeated precipitation results in far less coprecipitation of the impurity since the concentration of the contaminant in the second solution from which reprecipitation takes place is much less than in the original solution. Reprecipitation is feasible in the case of hydrous oxides (hydroxides) which may be redissolved easily, but some precipitates, barium sulfate for example, do not lend themselves to "double precipitation" since they do not readily dissolve in any of the usual solvents.

Since adsorption is a function of surface area, and since digestion causes the formation of fewer and larger crystals, coprecipitation due to surface adsorption or to occlusion usually may be reduced by heating the precipitate in contact with the mother liquor. Furthermore, adsorp-

tion in general decreases with elevated temperature; therefore digestion at higher temperatures is advantageous.

It has already been mentioned that the order in which the reacting substances are brought together is sometimes important. The procedure for carrying out any routine analysis usually has been worked out so that a minimum of coprecipitation is encountered. In investigating a new method involving a precipitation one should be on the alert for coprecipitation errors. In any new study it must be remembered that just because an ion is or is not coprecipitated under one set of conditions is no reason that it will or will not contaminate even the same primary precipitate under another set of conditions. Once the facts regarding the existence and the extent of coprecipitation have been established, means possibly may be found to correct the situation. If not, and if the error exceeds allowable limits, a new procedure must be developed.

Questions and Problems

1. Explain the circumstances under which a salt precipitate will be dissolved by a strong acid.
2. Explain why the addition of an electrolyte to the wash water may prevent the peptization of a precipitate. What two particular properties must the electrolyte possess in order that its use will introduce no error in the analysis?
3. What effect will a change of temperature have on the solubility product of the majority of salts?
4. Why, as a rule, is the filtration of a precipitate an easier matter if the precipitating reagent is added slowly and with stirring than if added all at once?
5. Explain the advantage of digesting a precipitate prior to filtration. Under what condition would a long period of digestion be a disadvantage?
6. Show that a slightly soluble salt of the A_2B_3 type has a solubility product equal to $4X^5/9$ where X is the concentration of the $B^{=}$ ion.
7. The compound AB_2 is twice as soluble at a temperature of 30° as it is at 20°. How much greater will its solubility product be at the higher temperature?
   Answer: 8 fold greater.
8. If 0.0025 g. of the compound A_2B_3, having a molecular weight of 250, saturates a liter of solution, what is its solubility product constant?
   Answer: 1.1×10^{-23}.
9. The slightly soluble compound AB_2 has a molecular weight of 200 and is soluble to the extent of 5.0×10^{-4} moles per liter. (a) Calculate the solubility product. (b) How many milligrams of the compound remain dissolved per 100 ml. of solution if an excess concentration of A^{++} ion equal to 0.01 *M* is added? (c) How many milligrams of AB_2 will be lost if the precipitate is washed with 100 ml. of pure water?
   Answer: (a) 5.0×10^{-10}; (b) 2.2 mg.; (c) 10 mg.
10. (a) The solubility product of the slightly soluble hydroxide, $Me(OH)_2$, is 1.28×10^{-12}. If a solution of sodium hydroxide is slowly added to an acidified solution which is 0.02 *M* with respect to Me^{++} ion, at what pH will the

$Me(OH)_2$ begin to precipitate? (b) If 1.07 g. of ammonium chloride is added to 50 ml. of a solution which is 0.4 *M* with respect to NH_4OH, and this is poured into 50 ml. of solution which is 0.0079 *M* with respect to Me^{++} ion, will $Me(OH)_2$ precipitate or not? (Assume a total volume of 100 ml. after pouring the two solutions together.)

Answer: (a) 8.9; (b) no precipitate, saturated solution.

11. At what pH will a 0.030 *M* solution of ferric sulfate begin to precipitate $Fe(OH)_3$? $K_{s.p.}$ for $Fe(OH)_3 = 1.1 \times 10^{-36}$.

Answer: 2.5.

12. Calculate the pH of a buffer solution which will allow the precipitation of all the cobalt except 0.1 mg. when 250 ml. of a 0.05 *M* solution of cobalt chloride is saturated with hydrogen sulfide at room temperature. $K_{s.p.}$ for $CoS = 1.9 \times 10^{-27}$.

Answer: 0.70.

13. Calculate the solubility, in g. per 100 ml., of silver chromate in a 0.005 *M* solution of silver nitrate and in a 0.005 *M* solution of sodium chromate. $K_{s.p.}$ for $Ag_2CrO_4 = 2.0 \times 10^{-12}$.

Answer: 2.7×10^{-6}; 3.3×10^{-4}.

Chapter 15

GRAVIMETRIC ANALYSIS. EXPERIMENTAL

Determination of Chlorine in a Soluble Chloride

The chloride is dissolved, the solution acidified with dilute nitric acid and the anion is precipitated with silver nitrate. The precipitate of silver chloride,

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow$$

is coagulated by digesting and then is filtered, washed, dried and weighed to a constant weight (see p. 15). The precipitate can be filtered through a filter paper and ignited to burn the paper to a "weightless" ash; this results in the reduction of a large part of the silver chloride to silver by the carbon of the paper and necessitates the reconversion of the reduced silver to silver chloride by treatment with aqua regia. This procedure is not recommended since the use of the Gooch crucible, or any type of filtering crucible, eliminates the extra step necessitated by the reduction occurring during ignition. With the Gooch crucible the precipitate of silver chloride may be filtered, washed, dried and weighed immediately.

The method given for the determination of chloride obviously may be employed for the determination of silver; in addition, it may be applied to the determination of any ion the silver salt of which is insoluble in solutions slightly acidified with nitric acid. These include the halides, bromide and iodide (the silver salts of which are even less soluble than silver chloride) and cyanide and thiocyanate. Furthermore, hypochlorite, chlorite, chlorate, hypobromite, bromate, hypoiodite, iodate and periodate ions may be reduced with sulfurous acid to the corresponding halide, after which they too may be precipitated as the silver halide and the analysis carried out according to the procedure given below. Obviously, if any one of these ions is to be determined by this method, all others (that is, cyanide or thiocyanate, or any other halide) must be absent.

Procedure. Prepare Gooch crucibles or porous filtering crucibles as described on p. 10, dry them at 105° and weigh to a constant weight (see p. 15). Accurately weigh out samples of between 0.2 and 0.4 g. of the dry, finely divided chloride and transfer quantitatively to 250 ml. beakers. Dissolve in 150 ml. of chloride-free water and add 8 or 10 drops of concentrated nitric acid. Calculate the volume of 5 per cent silver

nitrate solution necessary to precipitate the chloride in the sample, assuming it to be pure sodium chloride. To the cold solution, and with constant stirring, add this amount of silver nitrate plus a 5 per cent excess or a 3 ml. excess (see p. 224), whichever is the greater. Cover with a watch glass and heat until almost boiling; then transfer to a hot plate or a steam bath and digest until, after stirring, the precipitate quickly settles. Then test for completeness of precipitation by adding a drop or two of silver nitrate solution; add more silver nitrate if a fresh precipitate appears in the test.

Place the weighed Gooch crucible in the suction flask and connect to the vacuum pump (see Fig. 1). Then decant the supernatant liquid into the Gooch crucible and transfer the precipitate to the crucible as described on p. 10. When the transfer has been completed, wash the precipitate in the crucible, still using suction, with a dilute solution of nitric acid prepared by adding 1 ml. of 6 *N* nitric acid to 500 ml. of water. In filtering and in washing never fill the crucible more than three-quarters full. After six or eight such washings collect a wash portion which has just passed through the crucible in a small test tube; test for silver ion by adding 1 or 2 drops of dilute hydrochloric acid. The faintest cloudiness indicates the need for further washing. Before discarding the filtrate make a final test for completeness of precipitation by adding 1 ml. of silver nitrate solution. No further precipitate should be obtained, but if one does appear an excess of silver nitrate must be added and the newly formed precipitate digested and filtered through the same Gooch crucible.

When the precipitate is clean, as shown by a negative test for silver ion, place the crucibles with tongs in clean, dry 250 ml. beakers and dry in the oven at 105° for an hour or more. Cool in the desiccator and weigh to the fourth decimal place. Return to the oven at 105° for 30 minutes, then cool and weigh again. Repeat the 30-minute drying period and the weighing as many times as is necessary to obtain a "constant" weight; that is, until two successive weighings are within 0.3 mg. of one another. From the weight of the precipitate of silver chloride calculate the percentage of chlorine in the sample. Duplicate results should show a deviation from the mean no greater than 3 parts per 1000.

Notes. In computing the amount of silver nitrate solution necessary to precipitate all of the chloride in the sample, it is safest to base the calculation on the assumption that the unknown is sodium chloride. Since sodium is one of the lightest of metals, it follows that the quantity of silver nitrate necessary to precipitate the chloride in a given weight of sodium chloride will be more than sufficient to precipitate that in the same weight of the chloride of a heavier metal. In this way the risk of later discovering that too little precipitating reagent had been added originally is practically eliminated. However, if it is thought that the unknown contains only a small percentage of chloride it is better to make no calculation of the amount of silver nitrate to be added, but rather to add the reagent until no

further precipitation is visible, thus avoiding the salt effect (see pp. 227–230) which might introduce a negative error.

Test the distilled water to see whether or not it is chloride-free by adding to a few milliliters of the water in a test tube a crystal of silver nitrate. A cloudiness indicates the presence of chloride ion. In that case consult the instructor.

The solution of the chloride is acidified with nitric acid to prevent the precipitation of other anions which might be present, the silver salts of which are insoluble in neutral solutions but which are soluble in acid solutions (e.g., carbonates and phosphates). The solution of the chloride must not be heated, once it has been acidified, until after an excess of silver nitrate has been added; otherwise a loss of chlorine will result because of either or both of the reactions: $Cl^- + H^+ \rightarrow HCl$, and $6H^+ + 6Cl^- + 2HNO_3 \rightarrow 3Cl_2 + 2NO + 4H_2O$.

The decomposition of silver chloride is catalyzed by light. In direct sunlight the action is rapid. Therefore the precipitate should be shielded from bright light. The superficial bluish color which the precipitate assumes is due to the metallic silver from this decomposition, but in diffused light the effect on the weight of the precipitate is not significant. Note that if the suspension of the precipitate is exposed to bright light before being filtered, the error will be negative if the solution surrounding the precipitate contains excess chloride ion (as in a determination of silver), but will be positive when the solution surrounding the precipitate contains excess silver ion (as in a determination of chlorine). In the former case the decomposition due to light results simply in a loss of chlorine, but in the latter situation the chlorine from the decomposition of silver chloride reacts with excess silver ion, giving additional silver chloride. The net gain then will be a silver atom for every molecule of silver chloride which was decomposed and then re-formed.

Since this experiment is often the first precipitation-gravimetric determination which the student performs, the importance of washing the precipitate until free from contamination is frequently not fully appreciated. The slightest cloudiness indicates the need for further washing. Though other ions are present in the liquid from which the precipitate is filtered, it may be assumed safely that when the wash solution shows no test for silver ion the precipitate is also clean in respect to other ions.

Washing is carried out with water slightly acidic with nitric acid in order to prevent peptization, as explained on p. 11. The small amount of nitric acid remaining with the precipitate after the washing is completed is volatilized during the drying which follows. So also would hydrochloric acid, which could be used in dilute solution for the washing *if* silver and not chlorine were being determined; in this case it has the advantage over a nitric acid wash solution of decreasing the solubility of the precipitate due to the common ion effect.

It is better never to fill the Gooch crucible entirely full of liquid. This will insure a clean portion of the crucible where it may be grasped with the tongs without loss of precipitate.

The initial period for drying the crucible and precipitate in the oven may be shortened if, after washing the precipitate, two rinses of alcohol are passed through the crucible followed by two of ether.

Calculation of Percentage of Chlorine. The precipitate which is weighed consists of silver chloride, AgCl. Since there is one atom of chlorine with an atomic weight of 35.46 in each molecule of silver chloride, molecular weight 143.3, it follows that chlorine constitutes 35.46/143.3 of the weight of the precipitate. This fraction of the weight of the precipitate divided by the weight of the original sample and multiplied by 100 will give the percentage of chlorine.

Suppose, for example, a chloride sample weighing 0.2023 g. yields a precipitate of silver chloride weighing 0.4951 g. The percentage of chlorine in the sample then is

$$\frac{(35.46)(0.4951)(100)}{(143.3)(0.2023)} = 60.58\%$$

Determination of Sulfur in a Soluble Sulfate

The principle involved in the gravimetric determination of sulfur is quite simple, being the precipitation of the sulfur in the form of barium sulfate, filtering the precipitate and finally weighing the barium sulfate. However, few gravimetric determinations are so fraught with possible errors. Barium sulfate tends to coprecipitate (see pp. 238–246) many contaminants, and the error thus introduced may be either positive or negative, depending upon the nature of the impurity coming out with the precipitate. Anions like chloride, chlorate and nitrate, if present when barium sulfate is precipitated, are coprecipitated as the corresponding barium salts in varying amounts depending upon the conditions (concentration, order of bringing reagents together, etc.), and cause high results. Many cations also may be coprecipitated; the alkali metals and calcium and ferric iron are brought down with the barium sulfate in the form of their sulfates. Coprecipitated cations almost always cause low results if sulfate is being determined because the molecular weight of the contaminating sulfate is lower than that of barium sulfate. If ammonium ion is present when barium sulfate is precipitated the negative error is especially pronounced because the ammonium sulfate which is coprecipitated will be completely volatilized upon ignition (the final step before weighing). During ignition the composition of many coprecipitated substances changes; for example, ferric sulfate is converted to ferric oxide, and this always causes low results in sulfate determinations. The fact that fairly accurate results may be obtained comes from careful attention to the details of a procedure which has been worked out with two ends in view—namely, to reduce, as much as possible, coprecipitation of foreign substances, and to effect a compensation of positive and negative errors which cannot be avoided entirely.

Because barium sulfate, practically speaking, is insoluble in all solvents, the process of reprecipitation as a means of purifying the precipitate cannot be employed. When it has been established that certain ions known to coprecipitate with barium sulfate are present in the sample for analysis, steps should be taken when possible to remove such ions before the barium sulfate is precipitated. For example, nitrate ion may be removed by acidifying the solution of the sample with hydrochloric acid and evaporating. Errors due to the presence of ferric ion may be reduced in three ways. The iron can be removed by precipitation as ferric hy-

droxide and the sulfate then determined in the absence of ferric iron. The ferric iron may be reduced to ferrous iron and the barium sulfate precipitated in the presence of the latter. This reduces the error since ferrous iron does not coprecipitate with barium sulfate so badly as does ferric iron. Again, the ferric iron can be converted into a complex ion by tartaric acid and thus reduce the extent of coprecipitation.

A great deal has been published regarding the errors commonly encountered in the gravimetric determination of sulfur (or barium) and the various methods of combating or minimizing these errors. A comprehensive survey of the matter may be found elsewhere.[1] The procedure given below is suitable for the analysis of a soluble sulfate in a solution not containing significant concentrations of the worst offenders among the coprecipitating ions. Calcium and ferric iron, and nitrates and chlorates must be absent.

Procedure. Accurately weigh out samples of about 0.5 g. and quantitatively transfer to 600 ml. beakers. See that the beakers have no scratches inside which would become impregnated with precipitate; also make sure that stirring rods have smooth ends. Add 50 ml. of water and if the sample does not completely dissolve add concentrated hydrochloric acid dropwise and warm until the solution is clear. Add 2 ml. excess of concentrated hydrochloric acid and dilute the solution to about 350 ml. Calculate the amount of 1 per cent barium chloride solution necessary to precipitate the sulfate in the sample, assuming it to be pure sodium sulfate; to the hot solution of the sample add this amount plus a 5 per cent excess, quickly and with rapid stirring. While still hot place over a steam bath and after the precipitate has settled add 1 ml. of the barium chloride solution to test for completeness of precipitation. If necessary, add more barium chloride, stir, digest, allow to settle and test again. When certain that an excess of the precipitating reagent has been added, place on the steam bath or over a low flame for an hour or longer.

When the supernatant liquid is clear decant it through an ashless filter paper. Test this filtrate with 1 ml. of barium chloride solution; do not conclude that all of the sulfate has been precipitated unless no cloudiness appears after standing 15 minutes; barium sulfate precipitates only slowly from very dilute sulfate solutions. Place a new beaker under the funnel (then if a leak occurs there will be less to refilter) and transfer the precipitate to the filter paper as directed on p. 10. The last bit of precipitate may be removed from the beaker by using a policeman, or the following method may be employed: With a piece of ashless filter paper about the size of a postage stamp wipe off the film of precipitate from inside the beaker and drop the paper into the funnel. Two or three

[1] See Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, 1943, Chap. XX.

pieces of paper should be sufficient to clean the barium sulfate entirely from the beaker, and from the stirring rod as well.

Wash the precipitate about 10 times with hot water, each time filling the filter cone almost full of water and allowing complete drainage before adding the next wash portion (see p. 12). Collect a small amount of washings in a test tube and add a few drops of silver nitrate solution. If a precipitate forms, the washing must be continued until finally the barium sulfate is free of chloride ion. It then may be assumed that the precipitate is clean.

Place the funnel containing the filter paper and precipitate in the oven for a few minutes; when partially dried remove the paper from the funnel and carefully fold into a bundle, place in a previously weighed porcelain or platinum crucible, char and ignite to a white ash. The details of these several steps are described on p. 14. During the ignition some of the barium sulfate might have been converted into barium oxide or barium sulfide. To remedy this add to the precipitate with a dropper enough 1:10 sulfuric acid to dampen the entire mass (about 8 or 10 drops). Then with a very low flame located some 10 cm. underneath the crucible *cautiously* warm until sulfuric acid fumes slowly are given off. (Haste makes waste here; if spattering occurs because of too high a temperature the entire determination will have to be repeated.) When all of the excess acid has been expelled, elevate the flame until the bottom half of the crucible glows at a faint red heat for 10 minutes. Then transfer to the desiccator to cool. Weigh the crucible and contents and repeat the 10-minute heating treatment, cool and weigh again. Repeat the heating and weighing until a constant weight is obtained. From the weight of the precipitate of barium sulfate calculate the percentage of sulfur, either as such or in terms of sulfur trioxide, in the sample. While a precision of 1 part per 1000 can be expected with some experience, a deviation of 3 parts per 1000 may be considered excellent for the beginner. The precision may well exceed the accuracy. If the sample contains ions which are particularly troublesome in coprecipitating, the error may amount to 15 or 20 parts per 1000.

Notes. The solution of the sample is acidified in order to prevent the simultaneous precipitation of other barium salts which are insoluble in neutral solutions, e.g., carbonate or phosphate. The solution must not be made too acidic since barium sulfate is somewhat soluble in dilute hydrochloric acid.

If the barium chloride is added slowly to the sulfate solution the occlusion of alkali sulfate predominates and this, as has been explained already, leads to low results. When the barium chloride solution is added rapidly some barium chloride is occluded, but while this causes a slight increase in the weight of the precipitate, the net result is quite close to the theoretical.

The crystals of freshly precipitated barium sulfate are extremely small; digestion causes the formation of larger crystals (see p. 8) and decreases the prob-

ability of leakage during the filtration. After filtering off the precipitate examine the filtrate carefully for small amounts of barium sulfate. Swirl the filtrate vigorously with a stirring rod; if any precipitate is present it may be detected as a "whirlwind" effect in the center of the rotating liquid.

During the ignition of the precipitate the decomposition of barium sulfate will take place to some extent if the temperature is too high: $BaSO_4 \rightarrow BaO + SO_3$. Furthermore, carbon from the filter paper may reduce some of the sulfate: $BaSO_4 + 2C \rightarrow BaS + 2CO_2$. Both BaO and BaS are reconverted to $BaSO_4$ by the treatment with sulfuric acid:

$$BaO + H_2SO_4 \rightarrow BaSO_4 + H_2O$$
$$BaS + H_2SO_4 \rightarrow BaSO_4 + H_2S$$

Determination of Sulfur in a Sulfide Ore

For the determination of sulfur in an insoluble sulfide—e.g., FeS_2—the sample must be rendered soluble either by treating with such reagents as aqua regia or bromine, or by fusion with such agents as sodium carbonate combined with potassium nitrate, or sodium peroxide. In either method the sulfide is oxidized to sulfate. In the former or wet method the reaction may be represented as

$$FeS_2 + 15Br + 3HNO_3 + 8H_2O \rightarrow Fe(NO_3)_3 + 2H_2SO_4 + 15HBr$$

In the fusion, or dry method, using sodium peroxide, the reaction is

$$2FeS_2 + 15Na_2O_2 \rightarrow 4Na_2SO_4 + Fe_2O_3 + 11Na_2O$$

In the wet method the oxidation takes place slowly and actually may be incomplete; and proper precautions are necessary to prevent or diminish coprecipitation resulting from the presence of nitrate and ferric iron (see discussion under the preceding section). The dry attack has some objectionable features too: large quantities of sodium or potassium are introduced and great care must be taken to avoid sulfur being taken up during the fusion from the gas of the burner. The latter may be avoided, of course, by electrical heating. The procedure given below utilizes the wet method and follows the principles of the Allen-Bishop procedure.[2]

Procedure. Accurately weigh dry, finely divided samples of pyrite of about 0.5 g. into 250 ml. beakers. Place the beakers containing the samples in a hood and to each add 4 ml. of bromine and 6 ml. of carbon tetrachloride and cover the beakers with watch glasses. Keep at room temperature for 15 minutes, stir occasionally and then add 10 ml. of concentrated nitric acid. Allow to stand again for 15 minutes with occasional stirring. Next, place on a steam bath and heat below 100° until the action has ceased and no more bromine fumes are evident. Remove the cover

[2] Allen and Bishop, *8th Intern. Congr. Applied Chem.*, 1-2, 48 (1912); Moore, *J. Ind. Eng. Chem.*, 11, 46 (1919).

from the beaker and continue heating on the steam bath until the solution has evaporated to dryness. Stir in 10 ml. of concentrated hydrochloric acid and heat at 105° in the oven for an hour. This will dehydrate the silica. Remove from the oven and add 2 ml. of concentrated hydrochloric acid, stir for a moment, and then add 50 ml. of water. Bring the solution to the boiling point and let simmer for 5 minutes. Cool, and add 2 g. of aluminum powder in order to reduce the iron. After the solution becomes colorless, cool, filter and wash the filter thoroughly. Receive the filtrate and washings in a liter beaker and dilute to 700 ml. Add 2 ml. of concentrated hydrochloric acid and 1 drop of stannous chloride to prevent atmospheric oxidation of the ferrous iron and heat the solution to boiling. Precipitate the sulfate by adding 50 ml. of 5 per cent barium chloride solution dropwise and allow the precipitate to settle for an hour or longer. Then continue with the procedure as described for the determination of sulfur in a soluble sulfate. Calculate the percentage of sulfur in the ore. The deviation from the mean should be under 4 parts per 1000.

Determination of Sulfur in Coal. Eschka Method

Procedure. Accurately weigh samples of about 1 g. of powdered coal. Mix with 3 g. of Eschka's compound, consisting of 2 parts of magnesium oxide and 1 part of anhydrous sodium carbonate. Place the mixture in a platinum crucible and cover with an additional 2 g. of Eschka's compound. Protect the crucible from the flame of the burner by a shield and heat the crucible. Better still, heat the crucible in an electric furnace to avoid completely contamination by sulfur-containing fuel gases. Apply the heat gradually to expel volatile matter. Stir the mixture occasionally with a platinum wire. After 30 minutes increase the heat to dull redness. Remove the crucible and cool when no carbon remains and the color of the mass is brown or yellow.

Place the crucible and contents in 100 ml. of water and heat to the simmering point for 30 minutes. Remove the crucible and rinse it, catching the rinse water in the beaker containing the solution. Then filter through a filter paper and wash the residue thoroughly, receiving the filtrate and washings in a 400 ml. beaker. Add 5 ml. of saturated bromine water and 1 ml. of 6 *N* hydrochloric acid. Boil gently for 10 minutes. (The bromine oxidizes any sulfites to sulfates.) When the solution is colorless cool the solution, add 2 drops of methyl orange and then dilute ammonium hydroxide until the solution is orange in color. Then add 1 ml. of 1 *N* hydrochloric acid and proceed with the precipitation by adding dropwise 20 ml. of 5 per cent barium chloride to the hot solution and continue as described for the determination of sulfur in soluble sulfates. Calculate the percentage of sulfur in the coal. For coals of about

2 per cent sulfur content the absolute deviation for duplicate determinations may amount to 0.05 per cent.

Determination of Phosphorus in Phosphate Rock

PHOSPHOMOLYBDATE METHOD

The gravimetric determination of phosphorus is accomplished by precipitating, from a solution alkaline with ammonium hydroxide, the hexahydrate of magnesium ammonium phosphate, $MgNH_4PO_4.6H_2O$. Although the precipitate may be dried at room temperature after washing with alcohol and ether, and weighed, the majority of analysts prefer to convert the precipitate by ignition into magnesium pyrophosphate and weigh in that form. The equations for the precipitation and ignition are:

$$PO_4^{\equiv} + Mg^{++} + NH_4^{+} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$$
$$2MgNH_4PO_4.6H_2O \rightarrow Mg_2P_2O_7 + 2NH_3 + 13H_2O$$

If the solution of the phosphate is acidic the value of $[PO_4^{\equiv}]$ will be relatively small since phosphoric acid ionizes in three steps and the third ionization constant is quite small. It follows that the concentration of the phosphate ion will be affected greatly by the pH of the solution and that the solubility of the magnesium ammonium phosphate will depend upon the hydrogen ion concentration. The precipitation therefore is accomplished by adding magnesium ion to the acid solution of the sample and then increasing the pH with ammonium hydroxide to the point where magnesium ammonium phosphate precipitates. However, the pH must not be sufficiently high for magnesium hydroxide to precipitate. Therefore, instead of simply adding a solution of a magnesium salt and ammonium hydroxide to the phosphate solution, "magnesia mixture" and ammonium hydroxide are used. The former consists of magnesium and ammonium chlorides and furnishes both of the cations needed to precipitate the magnesium ammonium phosphate. Because the ammonium ion decreases the hydroxyl ion concentration when the base is added, magnesium hydroxide does not precipitate.

The hydrates of magnesium hydrogen phosphate, $MgHPO_4$, and the normal salt, $Mg_3(PO_4)_2$, are prone to separate out in significant amounts along with the $MgNH_4PO_4.6H_2O$, unless the ionic concentrations are carefully controlled. If the precipitate is to be weighed as such without ignition to the pyrophosphate, a procedure sometimes followed, it is evident that a pure precipitation must be brought about. This may be done by dissolving the precipitate in acid and reprecipitating from the new solution wherein the concentrations of the ions, including hydrogen ion, are kept within narrower limits.

Since nearly all metallic ions yield precipitates with ammoniacal magnesium chloride, it is imperative that before the magnesium ammonium phosphate is precipitated all cations other than magnesium, ammonium and the alkalies must be absent. In the analysis of phosphate rock, fertilizers and the like it is necessary therefore to separate the phosphorus from interfering ions. This is brought about best by precipitating the phosphorus as ammonium phosphomolybdate from a nitric acid solution.

$$PO_4^{\equiv} + 3NH_4^+ + 12MoO_4^{=} + 24H^+ \rightarrow (NH_4)_3PO_4.12MoO_3 + 12H_2O$$

The "yellow precipitate" does not always correspond to the formula given in the above equation; therefore this precipitate is not weighed for the estimation of phosphorus. However, since it contains all of the phosphorus it is the means of separating the element from many interfering ions such as invariably are present in phosphate ores. The yellow precipitate can then be dissolved in ammonium hydroxide and magnesium ammonium phosphate then precipitated and ignited as already described. When highest accuracy is not necessary the yellow precipitate may be dissolved in a measured excess of standard sodium hydroxide solution and the excess base determined by titration with a standard acid solution. Fertilizers, steel and alloys are so analyzed for phosphorus. The reaction with sodium hydroxide is:

$$(NH_4)_3PO_4.12MoO_3 + 23NaOH \rightarrow 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O$$

or simply

$$(NH_4)_3PO_4.12MoO_3 + 23OH^- \rightarrow 3NH_4^+ + 12MoO_4^{=} + HPO_4^{=} + 11H_2O$$

In the analysis of a phosphate sample which does not contain interfering ions it is not necessary, of course, to precipitate the molybdate; rather the magnesium ammonium phosphate may be precipitated directly.

Procedure. Before beginning the procedure prepare the following solutions which will be needed during the course of the analysis:

Magnesia Mixture. Dissolve 50 g. of magnesium chloride hexahydrate and 100 g. of ammonium chloride in 500 ml. of water. Add ammonium hydroxide until *slightly* alkaline and filter after 24 hours. Acidify with hydrochloric acid and add 5 ml. of concentrated hydrochloric acid in excess. Dilute to 1 l.

Ammonium Molybdate. Make up each of the following solutions: (a) Dissolve 120 g. of molybdic acid (80 per cent MoO_3) in a solution of 80 ml. of concentrated ammonium hydroxide in 400 ml. of water. (b) Add 400 ml. of concentrated nitric acid to 600 ml. of water. Pour solutions

(a) and (b) together, let stand overnight or longer, decant from any sediment and preserve the clear solution in a glass-stoppered bottle.

ALKALINE CITRATE SOLUTION. Dissolve 5 g. of citric acid in 140 ml. of water and add 70 ml. of concentrated ammonium hydroxide.

Accurately weigh samples of about 0.25 g. of the dry, finely divided material for analysis. Place in 150 ml. beakers, add 5 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid. Cover the beakers with watch glasses and heat with a very low flame or on a hot plate until only a few milliliters of viscous liquid remains. Then add 0.2 g. of boric acid and 10 ml. of 1:10 nitric acid. Heat until the solution boils and filter through a 7 cm. filter paper into a 250 ml. beaker. Wash the residue with five successive portions of 10 ml. of water each, catching the washings in the beaker containing the filtrate.

To the filtrate slowly add concentrated ammonium hydroxide until a slight precipitate is produced. Then add concentrated nitric acid dropwise and with stirring (use a thermometer as a stirring rod) until the precipitate just redissolves; then heat the solution to 60° and add 75 ml. of warm ammonium molybdate reagent. Digest the precipitate which forms for 30 minutes at 60°, stirring frequently. Put aside at room temperature and as soon as the precipitate has settled sufficiently test for complete precipitation by adding 1 ml. of the molybdate reagent to the clear, supernatant liquid. If additional precipitate forms, add more molybdate solution, digest and test again. Allow the precipitate to stand in contact with the solution for 4 hours, after which filter and wash the precipitate by decantation with three 10 ml. portions of 5 per cent ammonium nitrate solution. Place the beaker which still contains nearly all of the precipitate underneath the funnel and dissolve the precipitate by pouring a total of 20 ml. of the alkaline citrate solution through the filter. Then wash the filter with three portions of warm 1:20 ammonium hydroxide, and three portions of 1:10 hydrochloric acid. The total volume at this point must not exceed 150 ml. Add 2 drops of methyl red indicator and then concentrated hydrochloric acid until the color changes from yellow to pink; then add 1 ml. of the acid in excess. (Add the acid slowly and with stirring: if the yellow precipitate re-forms add more ammonium hydroxide and neutralize with acid again.)

Cool the slightly acid solution in ice and add 10 ml. of magnesia mixture and then concentrated ammonium hydroxide solution slowly and with stirring until the solution is alkaline. Now add 5 ml. in excess. The white precipitate which appears is magnesium ammonium phosphate hexahydrate. Allow it to settle several hours or overnight.

Filter through a filter paper and wash three or four times by decantation with cold 1:20 ammonium hydroxide, retaining most of the precipitate in the beaker. Then place this beaker under the funnel and wash

the filter with 50 ml. of warm 1:10 hydrochloric acid. Follow with five washings of the filter with small portions of 1:20 hydrochloric acid. From the cold combined filtrate and washings reprecipitate the magnesium ammonium phosphate hexahydrate by adding first 2 ml. of magnesia mixture and then freshly filtered ammonium hydroxide, the latter 5 ml. in excess. Allow the precipitate to settle several hours or overnight, then filter and wash thoroughly with 1:20 ammonium hydroxide.

Partly dry the filter and precipitate and then transfer to a weighed platinum or porcelain crucible. Ignite over a moderate flame until no carbon is visible. Place the crucible in a muffle furnace at 1100° or heat it with a Meker burner for 1 hour. Cool in a desiccator and weigh. Repeat the heating for half-hour periods and the weighing until a constant weight is obtained. Calculate the percentage of phosphorus in terms of P_2O_5. In experienced hands the deviation from the mean of duplicate results will be under 5 parts per 1000; for the student running the analysis for the first time a deviation of 10 parts per 1000 is acceptable.

Notes. Phosphate rock usually contains fluorine; boric acid is added to the acid solution of the phosphate to convert fluorides to fluoboric acid, HBF_4, in which form fluorine does not interfere.

Ammonium phosphomolybdate precipitates tend to go into the colloidal state, but the tendency is less if the precipitation is effected at 60°. Do not heat much higher than 60° or the ammonium molybdate will yield molybdic anhydride, MoO_3, which then largely comes out with the desired precipitate.

The yellow precipitate is washed with a solution of ammonium nitrate to prevent peptization of the ammonium phosphomolybdate.

The ammonium citrate solution converts iron and tin into soluble complex compounds, thus preventing the precipitation of these metals as phosphates.

The double precipitation of magnesium ammonium phosphate is necessary because of the presence of molybdate in the initial precipitate.

DETERMINATION OF PHOSPHORUS BY SHORT METHOD[3]

The following method for determining phosphorus avoids the precipitation of ammonium phosphomolybdate. Calcium, the chief metallic constituent in phosphate rock, is kept in solution by the presence of citrate ion, and the phosphorus is precipitated as magnesium ammonium phosphate. Aluminum, calcium, fluorine, iron, manganese, titanium, silica, zinc and organic matter, in the quantities found in phosphate rock, do not interfere. A large excess of magnesia mixture must be added because the citrate ion converts a good part of the magnesium ion into a complex. Pyrophosphate also may be determined by this method.

Procedure. Accurately weigh out samples of the dry finely ground rock weighing about 0.3 to 0.5 g. into 250 ml. Erlenmeyer flasks. To each add 10 ml. of concentrated hydrochloric acid and 2 ml. of concentrated

[3] See Hoffman and Lundell, *J. Research Natl. Bur. Standards*, **19**, 59 (1937).

nitric acid. Cover the flasks with watch glasses and simmer for 30 minutes. Rinse off watch glasses, add 25 g. of ammonium citrate, 5 ml. of hydrochloric acid and then 75 ml. of the solution of magnesia mixture (p. 257). Add concentrated ammonium hydroxide carefully until the solution is neutral to litmus and then 2 ml. in excess. Dilute to 200 ml. with water, add a few glass beads, stopper and shake frequently during a 30-minute period. Then allow to stand overnight. Filter and wash the filter paper and flask once with 1:20 ammonium hydroxide. Discard the filtrate. Dissolve any precipitate still in the flask with 50 ml. of 1:4 hydrochloric acid; then pour the acid through the filter paper to dissolve the precipitate on the paper. Wash the flask and the paper with small portions of more 1:4 hydrochloric acid totaling about 50 ml. Add 0.3 g. of citric acid and 1 ml. of magnesia mixture to the solution. Add, while stirring, concentrated ammonium hydroxide until the solution is alkaline to litmus and then 5 ml. in excess. Stir frequently during a 30-minute period and then allow to stand for 4 hours or overnight.

Filter the precipitate of magnesium ammonium phosphate through an ashless filter paper and wash thoroughly with 1:20 ammonium hydroxide. Partially dry the precipitate and paper, transfer to a weighed platinum or porcelain crucible, char the paper at a low temperature and ignite to a constant weight with a Meker burner or in a muffle furnace. Calculate the percentage of phosphorus present in terms of P_2O_5. The precision should be as good as that obtained by the procedure of the ammonium phosphomolybdate method (p. 259).

Gravimetric Determination of Iron

After bringing the material into solution, iron may be determined by precipitating it as ferric hydroxide, or rather as hydrous ferric oxide, $Fe_2O_3.xH_2O$. The precipitate is filtered on paper and ignited to ferric oxide, Fe_2O_3, in which form it is weighed.

Hydrous ferric oxide is extremely insoluble; its incipient formation is of a colloidal nature but the presence of foreign ions causes it to coagulate into a gelatinous mass so that it can be filtered. The filtration will be slow, however, unless the coagulation is maintained. Washing by decantation, prior to filtration, is advisable, and a dilute solution of a volatile ammonium salt should be used in the washing. This will prevent the dispersion of the coagulated gel.

Hydrous oxides such as that of iron, being of a colloidal nature, possess a vast surface area so that they show a strong tendency toward the adsorption of foreign ions. Precipitated from an alkaline solution, hydrated ferric oxide adsorbs hydroxyl ions which, in turn, adsorb a secondary layer of cations. Contamination therefore must be prevented by double precipitation; this may be done since the precipitate ferric

oxide may be redissolved in acids. The second precipitation will yield a much less contaminated product (see Coprecipitation, p. 245).

Ignition of the hydrated ferric oxide requires particular care if accurate results are to be obtained. The paper must be charred slowly or the ferric oxide will be partly reduced to magnetic iron oxide, Fe_3O_4. A good circulation of air during the ignition will aid in preventing this. In addition, a sufficiently high temperature, close to 1000°, must be maintained to drive off the last trace of water which is rather tenaciously held.

Metals like aluminum, trivalent chromium and titanium must be absent since they also are precipitated by ammonium hydroxide. Anions such as arsenate, phosphate, vanadate and silicate cannot be tolerated for they form insoluble iron salts in weakly alkaline solutions. Furthermore, there are some other substances which interfere with the determination because they prevent the precipitation of iron by forming complex ions with the ferric ions—for example, organic hydroxy compounds such as tartaric and citric acids. These, however, may be destroyed by oxidation.

Procedure. The sample may be fairly pure iron itself, a soluble iron compound such as ferrous ammonium sulfate or an ore of iron. In the last case dissolve the sample in a manner described in the procedure for determining iron volumetrically (p. 191), but do not add any stannous chloride. If iron wire or filings comprise the sample it may be dissolved in dilute hydrochloric acid.

Accurately weigh samples of about 1 g. of ferrous ammonium sulfate, or of iron ore, or about 0.2 g. of iron wire or filings. Bring into solution, dilute to 50 ml., heat to boiling and add dropwise 1 ml. of concentrated nitric acid. Continue to boil gently for 5 minutes. The initial brown color is due to the formation of $FeSO_4.NO$, but this decomposes with the boiling and a yellow color appears.

Dilute the solution to 200 ml., heat almost to the boiling point and add freshly prepared 1:1 ammonium hydroxide (filter before using if any silica is present in the reagent bottle), while stirring constantly. An excess of ammonium hydroxide is assured if the odor of ammonia persists just above the beaker when the solution is boiling gently. Continue to boil for a minute or two after adding the hydroxide, then remove the flame and allow the hydrated ferric oxide precipitate to settle somewhat. Test the supernatant liquid by adding a few drops of ammonium hydroxide; note whether or not any additional precipitate is formed. If so add more ammonium hydroxide.

Decant the supernatant liquid through an ashless fast-filtering paper; retain the bulk of the precipitate in the beaker and wash by decantation four times with 50 ml. of hot water. Discard the washings and replace the beaker under the funnel with the one containing the bulk of the pre-

cipitate. Pour 50 ml. of 1 *N* hydrochloric acid into the filter paper so that it continuously wets the entire paper and then wash the filter with hot water until it is perfectly white. Remove the beaker containing the precipitate, the acid and washings, and heat. If necessary to bring all of the precipitate into solution add more 1 *N* hydrochloric acid. Add a few drops of nitric acid to insure all the iron being in the ferric state. Reprecipitate the hydrated ferric oxide by adding ammonium hydroxide as was done the first time. After the precipitate settles filter through the same filter paper as was used before, again washing by decantation but with hot ammonium nitrate solution, 4 g. to 500 ml. of water. Finally bring all of the precipitate into the filter paper (see p. 11) and continue to wash the precipitate and paper with ammonium nitrate solution until a test portion gives no precipitate with a few drops of silver nitrate solution.

When the precipitate has been washed clean, partly dry it by placing the funnel in the oven at 105° for (only) 10 minutes; then transfer it to a previously weighed porcelain crucible as directed on p. 15. Char the paper slowly and then ignite with the full heat of the burner, taking care to exclude the gases of the flame from the interior of the crucible. After 20 minutes no carbon should remain. Cool in the desiccator and weigh; then reheat for 15-minute periods until a constant weight is obtained. Calculate the percentage of iron in the sample in terms of Fe_2O_3. The average deviation from the mean result should be 5 parts per 1000 or less.

Notes. The 1 ml. of nitric acid is added in order to oxidize any ferrous iron to the ferric state. Should the precipitate come out with a greenish instead of a brick-red color, ferrous iron is indicated. In that case dissolve the precipitate by adding a little hydrochloric acid, and add another 1 ml. portion of nitric acid and boil gently for several minutes. Then reprecipitate by adding ammonium hydroxide.

The precipitate of hydrated ferric oxide must be washed immediately after filtering. If allowed to dry, the impurities become calked in the precipitate and are very difficult to wash out.

Hydrous metallic oxides are generally peptized by water. The first washing of the precipitate may be done with water (and the water may be hot since the precipitate has such a low solubility), for there are sufficient foreign ions present to prevent peptization. After the second precipitation, however, it is advisable to wash with a solution of ammonium nitrate.

The precipitate may be regarded as free from all contaminating ions when it has been washed free of chloride ion. Thus the chloride ion test, which is simple to make, may be used to indicate the elimination of impurities.

Analysis of Limestone

In analyzing a substance in regard to one particular constituent, as has been done in preceding experiments, any error which might be made detracts from the accuracy, but only in regard to the one constituent.

In the analysis of a substance such as limestone, and later, of brass, in which the composition in regard to a number of constituents is sought, it is evident that an error made at one point does not merely vitiate the result for the constituent being separated at the moment, but, in addition, might contribute to the error of all subsequent determinations. It follows that all of the proficiency which the student by now has come to command should be brought to bear upon each step as, one by one, the several constituents are separated and determined.

Limestone consists principally of calcium carbonate. It is the raw material used in the manufacture of lime and its analysis is widely performed in routine control work. In addition to calcium carbonate, limestones usually contain varying amounts of magnesium and smaller proportions of silica, iron, aluminum and manganese, and often phosphorus, sulfur, titanium and the alkalies. A scheme for the complete analysis of limestone may be found in Hillebrand and Lundell, *Applied Inorganic Analysis*, John Wiley & Sons, New York, 1929; in the "proximate"[4] analysis which follows, those constituents or components are determined which ordinarily are run in commercial laboratories. These include (a) loss on ignition (water, carbon dioxide and any organic matter), (b) silica, (c) R_2O_3 (the combined oxides of aluminum, iron, titanium, manganese and phosphorus), (d) calcium oxide, (e) magnesium oxide and (f) carbon dioxide.

DETERMINATION OF MOISTURE AND LOSS ON IGNITION

The sample must be collected and prepared for analysis in accord with the general rules already mentioned (see pp. 5–6). Accurately weigh samples of not more than 1 g. into platinum crucibles which previously have been ignited over the Meker burner or in a muffle furnace at 1000° to 1100° and weighed to a constant weight. Place in the drying oven at 105° to 110° for 2 hours, cool in the desiccator and weigh. Repeat the drying for 1-hour intervals and the intervening weighings until constant weight is obtained. Report the loss of weight as due to hygroscopic water.

After the determination of moisture the same samples may be used for the determination of loss on ignition. When the limestone is heated to around 1000° or 1100° the principal change taking place is the loss of carbon dioxide and "essential hydrogen" (hydrogen which in combined form is an integral part of the molecule) in the form of water. In addition,

[4] The determination of the elementary composition of a complex substance (such as limestone) is called the ultimate analysis of the substance, even though the constituent elements might be reported in terms of their oxides, for example. The proximate analysis involves the determination of the major constituents as radicals, or compounds, or even as mixtures—e.g., as moisture, ash, mixed oxides, etc. The term proximate does not imply any departure from the usual practices for attaining high precision and accuracy.

any organic matter which may be present is decomposed, and oxidations such as of sulfides to sulfates and ferrous iron to ferric iron will occur. The last two oxidations will cause a gain in weight; however, the loss in weight of a dry sample usually will give a measure of the carbon dioxide content with an accuracy of around 1 per cent.

Procedure. Use the residue from the moisture determination or weigh out new samples into platinum crucibles which previously have been heated to 1000° or 1100°, cooled and weighed to a constant weight. Cover the crucibles and heat over a Tirrill burner at a dull red heat for 5 minutes and then increase the heat to the full capacity of the burner for 5 minutes. Then replace the Tirrill burner with a Meker burner or blast lamp, or place in a muffle furnace at 1000° to 1100°. After 30 minutes cool in the desiccator and weigh; then heat again for 10-minute intervals, cool and weigh until a constant weight is obtained for each crucible. If the residue from the moisture determination was used, include the percentage of moisture in the result for loss on ignition. Keep the residue for subsequent determinations. Duplicate determinations should check within 0.2 per cent.

Notes. Porcelain crucibles may be used for the ignition but platinum crucibles are preferable. Porcelain will change weight at the high ignition temperature (platinum inappreciably). It is a good idea to reweigh the crucible after the material has been removed and the crucible cleaned, and to use this weight as the weight of the empty crucible. Porcelain crucibles, being rather thick, have the further disadvantage of being difficult to raise to the high temperature required if a Meker burner is used instead of the muffle furnace.

The crucible should be heated at a lower temperature at first in order to avoid a too rapid initial evolution of carbon dioxide. This might blow out fine particles of the limestone and cause erroneous results both here and in subsequent determinations.

After ignition the material is quite hygroscopic. Therefore the crucible should be kept covered and the weighing made as rapidly as possible (see p. 63).

DETERMINATION OF SILICA

The silica in the original sample of limestone may be present as such and in the form of insoluble silicates. The latter are rendered soluble by igniting with salts of sodium, potassium, calcium, etc., usually with sodium carbonate (p. 7). In the case of limestone the amount of calcium oxide obtained during the ignition of the sample is usually sufficient to convert the insoluble silicates into acid-soluble silicates. Since, furthermore, the quantity of silica in limestones generally is low, the addition of a flux is not necessary as a rule; but when the silica content is exceptionally high the proportion of calcium oxide may be insufficient to convert the silica into acid-soluble form. In such cases a fusion with sodium carbonate is necessary. The resulting sodium silicate (SiO_2 +

$Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$) may then be treated with hydrochloric acid, forming a precipitate of silicic acid. Dehydration of the silicic acid is necessary before it is filtered. This may be accomplished either by evaporating the mixture of silicic acid and silica to dryness and heating at 105° as in the procedure below, or by fuming with perchloric acid. When it is treated with water or dilute acid the gel tends somewhat to pass into a colloidal state. A double evaporation and dehydration at 105°, however, will diminish the dispersed phase to negligible proportions; that which escapes filtration is largely compensated for by small amounts of metallic oxides resulting from coprecipitation.

Procedure. Transfer the residue from the determination of loss on ignition to 150 ml. beakers. Add 1 or 2 ml. of 1:1 hydrochloric acid to the crucible to loosen any adhering particles and add to the solution in the beaker, being careful that none is lost in the transfer. Repeat the washing of the crucible with small portions of dilute acid until the quantitative transfer of all of the residue to the beaker is assured. Keep the total volume as small as possible. Add 5 ml. of concentrated acid to the beaker. Warm and stir the mixture until the disintegration is complete and then evaporate over a steam bath until dry. This may be hastened by occasionally breaking up the pasty mass with a stirring rod as it approaches dryness. When a dry, mealy powder is obtained place in the drying oven at 105° for an hour. Then remove from the oven and moisten the residue with 5 ml. of concentrated hydrochloric acid, and 5 minutes later add 25 ml. of water and heat on the steam bath to dissolve the acid-soluble substances present. Filter the residue of silica through a 7 cm. ashless filter paper and wash four times with hot 1:100 hydrochloric acid and then with hot water until free from chlorides, catching the filtrate in 400 ml. beakers. Unless the silica present is less than 5 or 10 mg., evaporate the filtrate to dryness, dehydrate and repeat the treatment with hydrochloric acid, the filtering and washing exactly as before. This double dehydration will regain the silica which went into solution during the first extraction. Reserve the filtrates and washings for succeeding determinations. Ignite the combined silica residues from the two dehydrations in platinum crucibles already weighed to constant weight, using Meker burners or a muffle furnace at 1000°. After obtaining constant weights calculate the percentage of crude silica in the sample. The duplicate results should not differ by more than 0.2 per cent.

Notes. A small amount of silica escapes filtration even with double dehydration. This loss is just about counterbalanced as a rule by coprecipitated iron and aluminum oxides. In the most exact analysis two corrections are necessary: (a) the silica which remained in solution after the above procedure was carried out must be recovered from the precipitate of "combined oxides" (see final note of next section); and (b) the amount of pure silica in the above crude silica must be

estimated. The latter may be done by treating the crude, moistened silica with 3 drops of 1:1 sulfuric and 5 ml. of hydrofluoric acids; the mixture is then evaporated and ignited in the platinum crucible to convert the metallic sulfates to oxides, and reweighed. The loss in weight obviously represents pure silica, since all SiO_2 was expelled in the form of SiF_4 during the evaporation and ignition which followed the hydrofluoric acid action ($2H_2F_2 + SiO_2 \rightarrow SiF_4\uparrow + 2H_2O$). The residue from the hydrofluoric acid treatment should be fused with a very small amount of sodium carbonate and the cake dissolved in hydrochloric acid and added to the main filtrate.

DETERMINATION OF COMBINED OXIDES

Ammonium hydroxide, added to the filtrate from the silica determination, precipitates the "combined oxides," consisting of hydrous oxides of iron, aluminum, titanium and manganese, and the phosphates of these metals. Any silica not previously removed will be precipitated here. The manganese is completely precipitated only if first oxidized; this is accomplished with bromine or ammonium persulfate and at the same time iron is oxidized to the ferric state. If the manganese were not precipitated here as hydrous manganese dioxide it would come out later with calcium or magnesium. Since aluminum is amphoteric, a large excess of ammonium hydroxide cannot be tolerated. A double precipitation is necessary for combined oxides because some calcium and magnesium are always coprecipitated. After redissolving the hydrous oxides in hydrochloric acid, they are reprecipitated from solutions obviously containing only little of the calcium and magnesium originally present. The second precipitation therefore yields the mixed oxides practically free from these metals.

Procedure. The filtrates from the silica determination should have a volume of 150 to 200 ml. Add to each about 1 g. of ammonium chloride so that sufficient ammonium ion will be present to prevent the precipitation of magnesium when ammonium hydroxide is added. Heat the solution to boiling and add 2 ml. of saturated bromine water and simmer for 3 minutes. To the hot solution add 2 drops of methyl red indicator and then carbonate-free concentrated ammonium hydroxide from a newly opened bottle (filter if necessary) until the solution is slightly alkaline. Boil the solution gently for 2 or 3 minutes and filter immediately through a small, ashless filter paper into 400 ml. beakers. Wash the precipitate twice with hot water, then place the filtrate to one side for future use. Place the original beaker under the funnel and pour over the filter paper 25 ml. of 3 *N* hot hydrochloric acid to dissolve the precipitate. Wash the paper five times with hot water. To the solution in the beaker, which should have a volume of around 75 ml., make a second precipitation of the hydrous oxides, using bromine water and ammonium hydroxide as before. Collect the precipitate on the same paper as was used after the

first precipitation and receive the filtrate in the beaker containing the first filtrate. Wash with 1 per cent ammonium nitrate solution until a small wash portion gives a negative test for chlorides. Do not test for cloudiness until after washing five times, and then use only 1 ml. for the test. (Begin the evaporation of the combined filtrates in preparation for the determination of calcium.) Place the filter paper containing the hydrous oxides in a weighed porcelain crucible, char the paper and ignite over a Meker burner and weigh to a constant weight. Calculate the percentage of "R_2O_3" in the sample. The results of duplicate analysis should agree within 0.2 per cent.

Notes. Bromine water is preferable to ammonium persulfate for oxidizing the manganese and iron in the solution since the use of the latter contributes sulfate ions. This would result in the coprecipitation of sulfate with the calcium oxalate when calcium is determined. The manganese is oxidized by bromine to MnO_2 which upon heating becomes Mn_3O_4.[5]

More than a slight excess of ammonium hydroxide in precipitating the hydrous oxides is objectionable for three reasons: it would cause some of the hydrous aluminum oxide to dissolve; it would react with bromine ($2NH_4^+ + 3Br_2 \rightarrow N_2 + 6Br^- + 8H^+$); and it would permit the precipitation of some calcium carbonate, since some carbon dioxide from the air is bound to enter the solution.

The ammonium hydroxide used should be carbonate-free.

For an ultimate analysis the elements present in the mixed oxides may be individually determined by dissolving the residue in hydrochloric acid, or fusing with potassium bisulfate, and separating in a manner similar to the procedure in qualitative analysis. If desired, the small amount of silica which escaped separation up to this point may be determined by dissolving the potassium bisulfate fusion of R_2O_3 in 1:10 sulfuric acid, evaporating to dehydrate the silica, taking up with dilute acid to dissolve the metallic sulfates and filtering off the silica. Ignite and weigh this residue and add to the corrected weight (after hydrofluoric acid treatment) of silica previously obtained.

DETERMINATION OF CALCIUM

At this stage in the analysis of limestone the solution (the combined filtrates from the R_2O_3 determination) contains calcium, magnesium, potassium and sodium cations, a great deal of the last if a sodium carbonate fusion was necessary in the beginning. Calcium is determined by precipitating calcium oxalate from an almost neutral solution. An easily filtrable precipitate is obtained by acidifying the solution, adding ammonium oxalate and then gradually increasing the pH by adding ammonium hydroxide. Unfortunately both sodium oxalate and magnesium oxalate coprecipitate with calcium oxalate. A double precipitation of calcium oxalate therefore is necessary. A considerable excess of ammonium oxalate must be added because the magnesium present (and in some limestones

[5] Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XII, Longmans, Green & Co., New York, 1932, pp. 221, 231.

it is present in considerable amounts) forms complex oxalate salts. The contamination of calcium oxalate by magnesium oxalate is decreased because of this complex ion formation and also because of the tendency of magnesium oxalate to form supersaturated solutions. From the latter fact it follows that prolonged digestion of the calcium oxalate precipitate is undesirable, since it might lead to postprecipitation of magnesium oxalate.

The precipitate of calcium oxalate may be treated in several ways before weighing. (a) The precipitate, $CaC_2O_4.H_2O$, can be dried at 105° and weighed as such, though this is not recommended. (b) If calcium oxalate is ignited at 500° ± 25° it is converted quantitatively into the carbonate. This procedure is recommended only if a muffle furnace in which the temperature can be controlled very accurately is available. (c) By treating the calcium oxalate with sulfuric acid it is converted into oxalic acid, which may be titrated with standard potassium permanganate solution; from the results of the titration the calcium present in the precipitate can be calculated (see p. 196). (d) The calcium oxalate may be treated with sulfuric acid and the resulting calcium sulfate weighed after expelling the excess acid. With proper care this method is very satisfactory. (e) Finally, the calcium oxalate may be ignited over a Meker burner or a blast lamp at which temperature it is converted into the oxide ($CaC_2O_4 \rightarrow CaO + CO_2 + CO$). This is perhaps the method most often employed. Calcium oxide is hygroscopic and must be weighed quickly in order to obtain a constant weight.

Procedure. The combined filtrates from the precipitation of the hydrous oxides should be evaporated if necessary to a volume of about 200 ml. Add 2 drops of methyl red indicator and acidify the solution with hydrochloric acid. Heat nearly to boiling and add a clear solution of 2 g. of ammonium oxalate dissolved in 25 ml. of water. Put the beaker over a low flame so as to keep the temperature of the solution at 70° to 90° and add dropwise 2 *N* ammonium hydroxide from a buret mounted above the beaker, stirring all the while. The addition of the base should take 10 or 15 minutes. When the solution is barely alkaline, set the beaker aside, cover with a watch glass and let stand. As soon as the precipitate of calcium oxalate has settled somewhat, test for completeness of precipitation by adding 1 ml. of ammonium oxalate solution. After an hour decant almost all of the supernatant liquid through a 7 cm. filter paper and wash the precipitate by decantation two or three times with cold water, receiving the filtrate and washings in a 600 ml. beaker. (Add 50 ml. of concentrated nitric acid to the filtrate and place it on the steam bath so that it may be evaporating while continuing the determination of calcium.) Put the beaker containing the bulk of the precipitate under the funnel and pour 25 ml. of 3 *N* hydrochloric acid over the entire sur-

face of the filter paper in order to dissolve the calcium oxalate on the filter. Then wash the paper thoroughly with hot water and dilute the filtrate to 250 ml. If the precipitate in the beaker has not completely dissolved, heat the solution until it does. When almost to the boiling point add about 0.5 g. of ammonium oxalate dissolved in 15 ml. of water and then add dropwise, as in the first precipitation, 2 *N* ammonium hydroxide until slightly alkaline, as indicated by methyl red. Cover with a watch glass and allow to stand for an hour.

(If calcium is to be determined volumetrically by titrating the acid solution of the precipitate with permanganate, filter the calcium oxalate through a Gooch crucible.) If the calcium is to be weighed in the form of calcium oxide, filter the precipitate through an ashless filter paper. After filtering wash thoroughly with a cold solution of ammonium oxalate, 5 g. to 1 l. of water. (Combine this filtrate and the washings with the first filtrate and continue the evaporation already started.) Place the paper containing the now clean precipitate in a weighed platinum crucible, char the paper slowly, then heat at a moderate temperature over a Tirrill burner and finally ignite at the full heat of a Meker burner or in a muffle furnace at about 1100° if one is available. Cool in the desiccator for only 20 minutes, or until at room temperature, and, with the crucible cover on, weigh as rapidly as possible (see p. 63). After constant weight is obtained calculate the percentage of calcium oxide in the sample. Duplicate results should not differ by more than 0.3 per cent.

Notes. Read p. 232 on the effect of the pH on the solubility of a salt like calcium oxalate and then explain the precipitation of this salt in the above determination as the solution is made slightly alkaline with ammonium hydroxide. This method of bringing about the precipitation not only promotes a texture of the precipitate which makes filtration easy, but also minimizes contamination from coprecipitation.

Calcium oxide, when exposed to air, not only will take up water but will combine with carbon dioxide to form calcium carbonate as well; thus the necessity for rapid weighing. It is so hygroscopic that if left overnight, for example, in a desiccator charged with calcium chloride, it may even gain weight. Therefore it should be left in such a desiccator only long enough to cool to room temperature. If it cannot be weighed immediately after cooling it should be kept in a desiccator containing a desiccant like magnesium perchlorate. See the discussion of desiccants, p. 17.

DETERMINATION OF MAGNESIUM

Magnesium is precipitated from an ammoniacal solution as magnesium ammonium phosphate hexahydrate, which upon ignition is converted to magnesium pyrophosphate. The general properties of the precipitate have been outlined under the discussion of the determination of phosphorus/p. 256. Because the hexahydrate tends to occlude ammonium salts and alkali oxalates it is necessary to treat the combined

filtrates from the calcium determination in a manner to eliminate or destroy the ammonium and oxalate ions which the solution contains. This is accomplished by evaporating the solution to dryness in the presence of nitric acid. Oxalates are thus oxidized to carbon dioxide and the ammonium ions to oxides of nitrogen and water.

Procedure. Add 50 ml. of concentrated nitric acid to the combined filtrates from the calcium determination if this has not already been done, and continue the evaporation to dryness. If a sizable residue remains it is probable that considerable ammonium salts are still present; in this case add a few milliliters of water, 25 ml. of concentrated nitric acid and 10 ml. of concentrated hydrochloric acid and repeat the evaporation to dryness. Take care to avoid spattering during the last stages of the evaporation. Then add 5 ml. of concentrated hydrochloric acid and 25 ml. of water, warm and stir. A slight precipitate of silica, coming largely from the solvent action of the several solutions upon glass vessels throughout the analyses, may be present. Filter through a very small filter paper, wash thoroughly with hot water and add the washings to the filtrate. Dilute the filtrate to about 150 ml. and cool the solution, preferably in ice. Dissolve 2 g. of diammonium hydrogen phosphate, $(NH_4)_2HPO_4$, in a small volume of water and add to the cold solution. Put in 2 drops of methyl red and add dropwise concentrated ammonium hydroxide until the indicator changes color; then add 5 ml. in excess. Stir the solution for several minutes and allow to stand overnight or at least 4 hours.

Filter through a filter paper and wash the precipitate by decantation three or four times with cold 1:20 ammonium hydroxide. Discard the washings. Place the beaker containing the major part of the precipitate under the funnel and pour upon the filter 50 ml. of warm 1:10 hydrochloric acid to dissolve the precipitate on the paper. Then wash well with 1:100 hydrochloric acid. If the volume of the solution in the beaker is not about 150 ml., dilute to that volume. Chill the solution and precipitate magnesium ammonium phosphate hexahydrate exactly as before. Let stand 4 hours or overnight and filter through an ashless filter paper. Then wash with 1:20 ammonium hydroxide until free from chlorides. Ignite the precipitate in a weighed platinum or porcelain crucible in the usual manner, using a Meker burner or a muffle furnace at 1000° to 1100°. After obtaining a constant weight for the magnesium pyrophosphate calculate the percentage of magnesium in the sample in terms of magnesium oxide. The results for duplicate determinations should agree within 0.3 per cent.

DETERMINATION OF CARBON DIOXIDE

Carbon dioxide is determined by treating a weighed sample of the limestone with excess acid and absorbing the liberated gas in a suitable

absorbing agent. The gain in weight of the vessel containing the absorbing material represents the weight of the carbon dioxide in the sample. Formerly a concentrated solution of potassium hydroxide was used to absorb the carbon dioxide, but the usual practice at present is to employ solid materials such as Ascarite, which is a mixture of sodium hydroxide and asbestos. It is obvious that the liberated carbon dioxide must be dried before it is absorbed, else the gain in weight of the absorption vessel would represent not the carbon dioxide alone, but moisture as well. Provision must be made, furthermore, to trap the water formed when the gas reacts with the sodium hydroxide during the absorption ($CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$), or the gain in weight would be less than the weight of the carbon dioxide. In addition, it is necessary to prevent any other gas which might be liberated when the sample is treated with acid from being taken up by the Ascarite. Hydrogen chloride from the acid used and sometimes hydrogen sulfide must be trapped out. All this necessitates a train of apparatus such as is shown in Fig. 36, the details of which will be explained presently.

This experiment is typical of gas absorptions in general. Other common examples are the determination of carbon and hydrogen in organic compounds. It is not difficult to make accurate analyses by gas absorption. It is imperative that the apparatus be gas-tight and that care be taken to make accurate weighings of the absorption vessel.

Anhydrous calcium chloride often has been used to dry the gas before it enters the absorption vessel. Others desiccants include: "Dehydrite," $Mg(ClO_4)_2.3H_2O$; "Anhydrone," $Mg(ClO_4)_2$; "Drierite," $CaSO_4$; and "Dessichlora," $Ba(ClO_4)_2$. Anhydrous calcium chloride is not recommended, for it frequently contains a small amount of calcium oxide which would absorb carbon dioxide. If it is used to dry the gas before the liberated carbon dioxide enters the absorption vessel it is necessary first to treat it with carbon dioxide in order to convert any calcium oxide to harmless calcium carbonate.

Apparatus. The apparatus is shown in Fig. 36. *C* is a wide-mouth generator flask in which the sample is placed. It is fitted with a two-hole rubber stopper. Inserted in the stopper is separatory funnel *B* which will contain hydrochloric acid; also condenser *D*. In the mouth of the separatory funnel a one-hole rubber stopper is placed and through it is mounted a calcium chloride tube of Ascarite, *A*. The condenser is connected through glass tube *E* to the train of U-tubes *F*, *G* and *H*. The U-tube *F* contains anhydrous copper sulfate at the bottom of the tube and a desiccant, say Anhydrone, in the top half of the two sides. Tube *G* is charged with Anhydrone alone. Tube *H* is the absorption vessel; it contains Ascarite for the most part but the side away from the generator flask contains some Anhydrone as shown in the figure. Across the top of

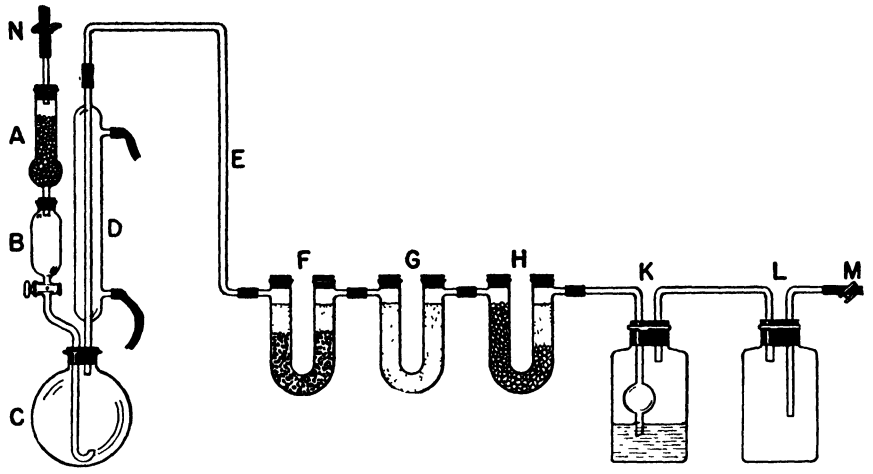


FIG. 36. Apparatus for the determination of carbon dioxide.

this tube a piece of copper wire may be attached to serve as a hook for suspending the U-tube from the balance stirrup when weighing. Cotton plugs should intervene between the two chemicals when more than one is placed in a single tube; cotton also is inserted at the top in each arm of the tubes to prevent dust from the absorbent or the desiccant from being carried along by the gas. Stoppers in the U-tubes should be corked tightly and coated with sealing wax. Better still, U-tubes equipped with ground-glass stopcocks may be used.

Tube *H* is connected to wide-mouth bottle *K* (containing a little sulfuric acid) by a glass tube which in turn is coupled to a tube dipping barely beneath the surface of the acid. The latter tube has an enlarged portion which serves to prevent any acid from being drawn back into tube *H* if the pressure in *K* happened to become greater than that in *H*. Bottle *K* in turn is connected by glass tubing to bottle *L* which acts as a trap for any water which might otherwise accidentally enter the train from the aspirator (not shown in the drawing) which joins *L* through heavy rubber tubing carrying pinchcock *M*. All units of the apparatus should be connected glass to glass without unnecessarily long pieces of rubber tubing between.

The apparatus is operated as follows: First it is tested for leaks. Pinchcock *N* is closed and the aspirator is turned on and pinchcock *M* is opened slightly. Bubbles will be seen in bottle *K*, but if the apparatus is without leaks the bubbles soon will cease. If they continue all joints must be examined until the leak is found and repaired.

The several units of the apparatus serve the following purposes: Separatory funnel *B* contains hydrochloric acid which may be intro-

duced slowly through its stopcock to generator flask *C* containing the sample. The resulting carbon dioxide passes into the condenser *D* which returns any steam to *C*. Through *E* the gas goes into U-tube *F* where water vapor is absorbed by the Anhydrone and any hydrogen chloride or hydrogen sulfide is trapped out by the anhydrous copper sulfate. Passing on to tube *G*, the gas is further dried by the Anhydrone in that tube. Thus as the gas leaves *G* it is pure, dry carbon dioxide. Entering *H* the carbon dioxide is absorbed by the Ascarite, and the water formed by the reaction of the carbon dioxide and sodium hydroxide is caught and retained by the Anhydrone in the top part of the right half of this tube. Thus U-tube *H* gains in weight by an amount equal to the weight of the carbon dioxide liberated from the sample. As already explained, bottle *K* indicates the speed with which the gas is being drawn through the apparatus; it also prevents any air from reaching tube *H* should the pressure momentarily fluctuate in *K*. Bottle *L* catches any water which might back-flow from the aspirator. The aspirator should not be turned off while evacuating the apparatus without first closing *M* and opening *N*, else water will be drawn back into the apparatus, though bottle *L* will trap it and prevent its going farther.

Procedure. When the apparatus has been proved gas-tight open pinchcock *N*, turn on the aspirator and regulate the sweep of air through the train by proper adjustment of pinchcock *M*. The rate should be such that two or three bubbles per second pass through *K*. After 10 minutes close *M* and turn off the stopcocks of U-tube *H*, or if it is not equipped with stopcocks disconnect *H*, and quickly cap its small exit tubes with short pieces of plugged rubber tubing or with policemen. Then weigh U-tube *H*, handling it with a piece of Kleenex. Return *H* to the train, sweep air through the apparatus for 10 minutes more and weigh U-tube *H* again. Repeat this until constant weight is obtained (within 0.4 mg.).

Place an accurately weighed sample of about 1 g. of dry, finely divided limestone in *C* and add about 25 ml. of water and several glass beads. The water must cover the end of the upturned tube in *C*. Put about 50 ml. of 1:1 hydrochloric acid in the separatory funnel. Disconnect the aspirator at *K* and slowly add acid from *B* through its stopcock. Bubbles should be seen in *K* at a rate of two or three per second. After all of the acid has been added to the flask, heat flask *C* until the solution boils gently and continue heating until the evolution of gas ceases. Turn off the flame, close pinchcock *M*, reconnect the aspirator and open pinchcock *M* slowly so that air is drawn (pinchcock *N* is open, of course) at a slow rate through the train. After this has continued for 30 minutes disconnect U-tube *H* and weigh it. The gain in weight represents the carbon dioxide in the sample. Repeat the determination with a new sample. Duplicate runs should agree within 0.3 per cent.

Note. Errors in weighing the U-tube may result because of variations in the amount of moisture on the glass surface of the tube. This error usually may be avoided by using a similar but slightly lighter U-tube, which has been exposed to the same atmosphere as has tube *H*, as a tare when making the weighing. If this is done the weight of the carbon dioxide is equal, of course, to the number of grams by which tube *H* exceeds its tare after the absorption, minus the number of grams by which tube *H* exceeds the tare before the absorption. In other words, the weight of the carbon dioxide is equal to the gain in weight of tube *H*.

Determination of Lead

Alloys or oxides containing lead usually may be dissolved with dilute nitric acid, though the peroxide, PbO_2, and red lead, Pb_3O_4, require in addition some hydrogen peroxide. After solution is effected evaporation will expel the excess nitric acid, and lead sulfate may be precipitated with sulfuric acid. Unless the nitric acid is driven off the solubility of the lead sulfate would be considerably greater. In order to reduce further the solubility of the precipitate, ethyl alcohol is added to the solution before filtering. The lead sulfate is filtered through a Gooch crucible and dried at 180° before weighing.

Procedure. Accurately weigh about 0.5 g. samples of the material and transfer to 250 ml. beakers. Unless the substance is a soluble salt of lead, add 50 ml. of 1:3 nitric acid and heat until the solution simmers. After the reaction has ceased, if a brown residue is still undissolved add 3 ml. of 3 per cent hydrogen peroxide or more if necessary to bring about complete solution. Add the peroxide slowly since a frothing will result. When the solution is clear, cool and add 25 ml. of 1:1 sulfuric acid and evaporate on a steam bath until the volume is approximately 15 ml. Then heat over a low flame or on a hot plate until the first sulfuric acid fumes appear. Cool, add 50 ml. of water, stir and add 75 ml. of 95 per cent ethyl alcohol. Stir and put aside for 2 hours and then filter through a Gooch crucible. Wash six or eight times by pouring 1:1 alcohol into the crucible until two-thirds full. Apply suction only slightly both in filtering and in washing. Dry the crucible and precipitate at 180° and weigh to a constant weight. Calculate the percentage of lead in the sample. Duplicate results should not differ by more than 0.2 per cent.

Organic Precipitants in Gravimetric Analysis

In the above determination of lead as lead sulfate, recourse was taken to the use of an organic solvent to decrease the solubility of the precipitate. Other organic solvents similarly employed are ether-alcohol solutions and amyl alcohol. Organic *precipitants* are sometimes used to precipitate inorganic ions. Usually such organometallic compounds have quite small solubilities; as a rule they are distinctly and highly colored; they almost always have high molecular weights so that small amounts

of metal yield rather large amounts of precipitate; and because the majority of organic precipitants are weak acids it is possible to command considerable control over the precipitation of their metallic salts by proper regulation of the pH. Though the advantage of these characteristics has been utilized in various analyses, there are certain disadvantages encountered. One is the fact that the organic precipitants often are of rather low solubility, even in organic solvents, with the result that there is danger of the precipitant itself separating out and contaminating the desired precipitate when an excess of the organic reagent is added. Another is that the metallic salt of the organic compound frequently is not wetted by water and this property causes the precipitate to creep during filtration. The latter is more an annoyance than a real difficulty. Furthermore, the action of the organic precipitants generally is not so specific toward a given metal as might be desired.

Nevertheless the number of such precipitants which have been employed in inorganic analysis is quite large, as may be seen by consulting special works on the subject.[6] To illustrate those more frequently used the following are briefly described: in addition, the procedures for the determination of two metals, nickel and aluminum, by precipitation as organometallic compounds will be given.

DIMETHYLGLYOXIME (DIACETYL-DIOXIME)

This reagent was used in the quantitative determination of nickel by Brunck[7] over 40 years ago. It is a weak acid having the formula $(CH_3C{=}NOH)_2$ which ionizes to yield one hydrogen ion. Divalent nickel therefore reacts with two molecules of the compound to yield

$$\begin{array}{ccc} CH_3C{=}NOH & & HON{=}CCH_3 \\ | & & | \\ CH_3C{=}NO{-}Ni{-}ON{=}CCH_3 & & \end{array}$$

a very insoluble red compound of which the nickel comprises 20.32 per cent (56.69/288.8 = 0.2032). Dimethylglyoxime often is referred to as a specific precipitant for nickel. However, palladium also is quantitatively precipitated by dimethylglyoxime, platinum is partly precipitated and gold is reduced by it. The pH should be kept low, for cupric ion tends to coprecipitate in alkaline solutions. With ores it is best as a rule to precipitate all of the hydrogen sulfide group of metals, if present, before precipitating nickel with dimethylglyoxime. Aluminum, cobalt, chromium, iron, manganese and zinc do not interfere with the precipitation of nickel

[6] See, e.g., Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis*, Elsevier Publishing Co., New York, 1940. Southern, *J. Chem. Education*, **18**, 238 (1941).

[7] Brunck, *Z. angew. Chem.*, **20**, 834 (1907).

dimethylglyoxime under the conditions outlined below. The greatest value of this method of determining nickel is that before this precipitant came into use a dependable analysis of nickel alloys or ores containing cobalt was practically impossible. The precipitant is added to a slightly acid solution of the ore or alloy and then a small excess of ammonium hydroxide causes the precipitate to appear. Tartaric or citric acid is added if metals which are precipitated by ammonium hydroxide are thought to be present.

Determination of Nickel in Steel. Dimethylglyoxime Method

Procedure. Accurately weigh out samples of steel turnings of about 1 g. Transfer to 400 ml. beakers, add 50 ml. of 1:1 hydrochloric acid and 10 ml. of 1:1 nitric acid and warm until solution is complete. Allow to simmer for several minutes until oxides of nitrogen are expelled. Then dilute to 150 ml. and add 6 g. of citric acid. Slowly add concentrated ammonium hydroxide until a piece of litmus paper touched lightly with the stirring rod shows that the solution is barely alkaline, and then add 1 ml. in excess. If necessary filter through a 7 cm. filter paper and wash the paper thoroughly, receiving the washings in the beaker containing the filtrate. Add 1:1 hydrochloric acid until the solution is just acid to litmus, then heat to 60° or 70° and pour in 20 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Now slowly add ammonium hydroxide until the solution is slightly basic and digest over a steam bath for an hour. Filter through a previously weighed Gooch crucible. Test the filtrate for completeness of precipitation by adding 4 or 5 ml. of dimethylglyoxime and digesting for 15 minutes. Wash the precipitate in the crucible until free of chlorides. Dry in the oven at 105°, cool in the desiccator and weigh. Repeat, heating in the oven for 20-minute periods, until a constant weigh is obtained. Calculate the percentage of nickel in the steel. The percentage of nickel in many steels will run from a fraction of 1 per cent to 2 or 3 per cent. Many stainless steels may contain as much as 10 per cent of nickel or more. Duplicate results should differ by not more than 0.05 per cent.

Notes. The pH of the solution must be carefully controlled. The nickel will not precipitate if the solution is too acidic, and any copper present will coprecipitate if it is too alkaline.

If the steel is known to contain a high percentage of nickel the amount of the precipitant needed for complete precipitation may exceed 20 ml. A simple calculation shows that 1 ml. of a 1 per cent solution of dimethylglyoxime will precipitate 2.5 mg. of nickel. A 1 g. sample of steel containing about 10 per cent nickel therefore would require approximately 40 ml. of precipitant. A large excess of precipitant, however, must be avoided, first because some of the dimethylglyoxime itself may precipitate from the aqueous solution, and secondly because too much alcohol in the solution will increase the solubility of the nickel dimethylglyoxime.

The tartaric or citric acid is necessary in order to convert the ferric iron into a complex which is not precipitated by ammonium hydroxide. Citric acid is preferable because of the possibility of acid ammonium tartrate precipitating.

During the filtration the crucible should not be filled more than two-thirds full due to the tendency of the precipitate to creep.

8-HYDROXYQUINOLINE (OXINE), C_9H_6NOH

Oxine acts as a precipitant for some two dozen metals, so that it might seem to have little value in quantitative analysis. However, by using buffers to control the pH of the solution certain separations can be made. Its chief use has been in the determination of magnesium and beryllium from ammoniacal solution. Many metals, including aluminum, may be precipitated with oxine from a buffered acetic acid solution. For details of the use of this compound in quantitative separations one may consult the literature.[8] The use of oxine as the precipitant for aluminum is given below.

Determination of Aluminum. Oxine Method

(In the absence of ions other than alkalies, calcium, magnesium and beryllium)

Aluminum is usually determined by precipitation as hydrous aluminum oxide in a manner similar to the gravimetric determination of iron. The oxine method has the advantage of being more rapid. It may be employed to isolate aluminum from magnesium, calcium and beryllium in solutions which are slightly acid. In basic solutions oxine separates aluminum from phosphorus, arsenic and fluorine, and in ammoniacal solutions containing hydrogen peroxide, from titanium and a number of other metals.

Procedure. Obtain a soluble sample and accurately weigh an amount which contains 0.03 to 0.05 g. of aluminum. Dissolve in 100 ml. of water, warm the solution to 70° or 80°, add 1 drop of concentrated hydrochloric acid and for each 3 mg. of aluminum thought to be present add 1 ml. of a 5 per cent solution of 8-hydroxyquinoline dissolved in 2 *N* acetic acid. If a precipitate appears add 25 ml. of 2 *N* ammonium acetate solution; if not, add the ammonium acetate solution until the first permanent precipitate is obtained and then 25 ml. more. A yellow color in the solution indicates an excess of the precipitant. Let stand 1 hour and filter through a weighed Gooch crucible. Wash with cold water until free of chlorides and dry at 120°. Weigh to a constant weight and calculate the

[8] Kolthoff and Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928); Lundell and Knowles, *J. Research Natl. Bur. Standards*, **3**, 91 (1929); Hahn and Vieweg, *Z. anal. Chem.*, **71**, 122 (1927); Southern, *J. Chem. Education*, **18**, 238 (1941); Hillebrand and Lundell, *Applied Inorganic Analysis*, John Wiley & Sons, New York, 1929, p. 114.

percentage of aluminum. The precipitate is $Al(C_9H_6ON)_3$. The average deviation from the mean should not exceed 3 parts per 1000.

AMMONIUM NITROSOPHENYLHYDROXYLAMINE (CUPFERRON), $C_6H_5N(NO)ONH_4$

Cupferron was originally believed[9] to be specific for ion and copper but it precipitates a number of metallic ions. The separation of iron, titanium, and zirconium from manganese, aluminum or nickel furnishes one example of the use of this precipitant.[10] For an excellent summary of the possibilities of cupferron in analytical work see the discussion given by Hillebrand and Lundell.[11]

ALPHANITROSOBETANAPTHOL, $C_{10}H_6(NO)OH$

This reagent precipitates a number of cations from slightly acidic solutions, including cobalt, copper and iron, and separates them from barium, calcium, strontium, manganese, nickel and zinc, among others. Its chief application has been in the precipitation of small amounts of cobalt in the presence of relatively high concentrations of nickel. Fales[12] warns that in cobalt analyses employing this reagent a blank always should be run.

ALPHABENZOINOXIME, $C_6H_5CH(OH)C(NOH)C_6H_5$

This compound will precipitate copper from slightly basic solutions. It also forms an insoluble compound with hexavalent molybdenum in acid solutions. It has been employed in the determination of copper in the presence of molybdenum[13] by precipitating the copper from ammoniacal solutions of steel containing both copper and molybdenum. The results are slightly high but are good, as checked against steels of known copper content, and the analysis can be completed in 1 hour, whereas by other methods from 3 to 6 hours are usually necessary.

Problems

1. A 0.3000 g. sample of a chloride, when dissolved and treated with excess silver nitrate, gives a precipitate weighing 0.5942 g. What is the percentage of chlorine in the substance?
   Answer: 49.00%.
2. A sample of potassium bromate weighing 0.3822 g. is reduced to potassium bromide, after which an excess of silver nitrate solution is added. The precipi-

[9] Baudisch, *Chem. Ztg.*, 33, 1298 (1909).
[10] Brown, *J. Am. Chem. Soc.*, 39, 2358 (1917).
[11] Hillebrand and Lundell, *op. cit.*
[12] See Fales and Kenny, *Inorganic Quantitative Analysis*, D. Appleton-Century Co., New York, 1939, p. 349.
[13] Kar, *Ind. Eng. Chem., Anal. Ed.*, 7, 193 (1935).

tate of silver bromide obtained weighs 0.4296 g. What is the percentage purity of the potassium bromate?

Answer: 99.95%.

3. A sample of 0.1000 g. of a pure oxide of iron is brought into solution and hydrous ferric oxide is precipitated. The weight of Fe_2O_3 obtained is 0.1111 g. Is the formula of the oxide FeO, Fe_2O_3 or Fe_3O_4?

4. A sample of iron ore weighing 1.000 g. is dissolved and the iron precipitated as hydrous ferric oxide. After ignition the precipitate weighs 0.3850 g. Calculate the percentage of iron in the ore in terms of (a) Fe, (b) Fe_3O_4 and (c) $FeSO_4.7H_2O$.

Answer: (a) 26.9%; (b) 37.2%; (c) 134.0%.

5. A sample of limestone weighing 1.208 g. yields a precipitate of magnesium ammonium phosphate which upon ignition is converted into $Mg_2P_2O_7$ weighing 0.5020 g. Calculate the percentage of magnesium in the limestone in terms of MgO.

Answer: 15.05%.

6. The solution of a 1.050 g. sample of a silicate yields 0.2515 g. of Fe_2O_3 and Al_2O_3. The oxides are dissolved and the iron is reduced to the ferrous state after which it requires 26.72 ml. of 0.1000 *N* potassium permanganate solution for oxidation. Calculate the percentage of Fe_3O_4 and Al_2O_3 in the silicate.

Answer: 19.64% Fe_3O_4; 3.63% Al_2O_3.

7. (a) The calcium in 0.9082 g. of a substance is determined by precipitating calcium oxalate and igniting the latter to CaO weighing 0.5888 g. Calculate the percentage present in terms of elementary calcium.

(b) If the calcium oxalate precipitate had been converted into $CaSO_4$ before weighing, what weight would have been obtained?

(c) If the calcium had been determined volumetrically by treating the calcium oxalate with sulfuric acid and titrating with 0.1000 *M* potassium permanganate solution, how many milliliters of the permanganate would have been required?

Answer: (a) 46.34%; (b) 1.430 g.; (c) 42.01 ml.

8. A 1.000 g. sample consists entirely of sodium chloride and sodium bromide. It is dissolved and an excess of silver nitrate solution is added. The precipitate formed weighs 2.265 g. Calculate the percentage of NaCl and NaBr in the mixture.

Answer: 70.2% NaCl; 29.8% NaBr.

9. A mixture weighing 0.5000 g. consists of NaCl and $FeSO_4(NH_4)_2SO_4.6H_2O$. The volume, in milliliters, of a barium chloride solution necessary to precipitate the sulfur is exactly equal to the percentage of iron in the sample. Calculate the number of grams per liter of $BaCl_2.2H_2O$ in the barium chloride solution. (In solving this problem it is necessary to look up the logarithm of two numbers only.)

Answer: 43.74 g.

10. A sample of $FeSO_4.7H_2O$ is dissolved and an excess of barium chloride is added. The barium sulfate precipitated weighs 0.1400 g. If an identical sample of $FeSO_4.7H_2O$ is oxidized in acid solution with a potassium dichromate solution, 1.000 ml. of which is capable of oxidizing 0.006700 g. of sodium oxalate, how many milliliters of the dichromate solution will be required?

Answer: 6.00 ml.

11. A sample consisting of a soluble chloride mixed with a soluble bromide is dissolved and an excess of silver nitrate is added. The resulting precipitate is found to weigh 0.6032 g. The precipitate is treated with chlorine gas which converts it completely into silver chloride. It is then found to weigh 0.4930 g. Calculate the percentage of silver in the original precipitate.
Answer: 61.52%.

Chapter 16

VOLUMETRIC ANALYSIS BY PRECIPITATION METHODS

PREREQUISITES for analysis by titration methods in general are: the rapid attainment of complete reaction between the standard solution and that of the unknown; the absence of side reactions which would nullify a fixed stoichiometric relationship between the two reactants; the abrupt appearance at or quite near the stoichiometric point of some property which visibly will mark the point of chemical equivalence for the reactants. In the case of reactions in which a precipitate is one of the products the completeness and the reaction velocity are satisfactory, and usually only one reaction takes place so that there exists a definite and known stoichiometric relationship. Furthermore, the precipitation of an ion as one of its insoluble compounds obviously must promote a great change in the concentration of that ion in the supernatant liquid after the stoichiometric point has been reached. However, the precipitation reactions which are adapted to a feasible indication of the stoichiometric point are relatively few. Those which are suitable may be classified into four groups. The detection of the end point for these precipitation titrations is made possible by the development immediately after the stoichiometric point of (1) a colored secondary precipitate, e.g., Mohr's method for chlorides; (2) a turbidity, e.g., Liebigs' cyanide method; (3) a colored soluble compound, e.g., Volhard's method for chlorides, bromides or iodides; and (4) the adsorption of certain organic dyes by those particles of the precipitate in a colloidal state, e.g., Fajan's method for determining halides. These four classes will now be discussed and actual analyses embodying the principle of each will be given.

SECONDARY PRECIPITATES AS THE INDICATOR

The Mohr method for the determination of chloride by titration with a standard solution of silver nitrate illustrates the use of a secondary colored precipitate to mark the end point. Only a very small concentration of chloride ion may be at equilibrium with silver ion which simultaneously is at equilibrium with chromate ion (see p. 234). If, therefore, a solution of a chromate is added to an unknown solution of chloride and the resulting solution is titrated with a silver nitrate solution, precipitation

of pure silver chloride takes place until the chloride ion concentration is reduced to a negligibly small value. Further addition of silver ion causes silver chromate to precipitate and the deep red color of that compound indicates the end point of the titration.

The concentration of chromate ion necessary to bring about the precipitation of the red silver chromate at the stoichiometric point for silver chloride is calculable. The $K_{s.p.}$ value for silver chloride is about 1×10^{-10} and for silver chromate is 2×10^{-12}. When chloride is titrated with silver nitrate solution the concentration of the silver ion at the stoichiometric point is $\sqrt{10^{-10}}$ or 10^{-5} moles per liter. When the silver ion concentration has this value the concentration of chromate ion necessary to precipitate the red silver chromate must slightly exceed 0.02 M because

$$[CrO_4^{=}] = \frac{K_{s.p.}}{[Ag^+]^2} = \frac{2 \times 10^{-12}}{(10^{-5})^2} = 0.02$$

However, if the unknown chloride solution is made 0.02 M with respect to chromate, the solution becomes colored so deeply yellow that the formation of a small amount of silver chromate immediately following the stoichiometric point is obscured; it is customary therefore to make the concentration of the chromate ion only about 0.003 M. Its concentration must not be much lower than this, however, for it is obvious that the smaller its value the greater must be that of the silver ion in order that $K_{s.p.}$ for silver chromate be exceeded. Suppose, for example, that the solution of the chloride were made 0.0001 M with respect to the chromate ion. The concentration of silver ion necessary to make the solution saturated with silver chromate would be

$$[Ag^+]^2 = \frac{2 \times 10^{-12}}{10^{-4}} = 2 \times 10^{-8}$$

$$[Ag^+] = 1.4 \times 10^{-4}$$

Now if the volume at the end of the titration were 100 ml. and if the silver nitrate solution were 0.1 M, the volume of excess silver nitrate needed to the point of silver chromate precipitation would be 0.14 ml. for if X be the excess volume of silver nitrate solution, in milliliters,

$$\frac{X}{100}(0.1) = 1.4 \times 10^{-4}$$

$$X = 0.14 \text{ ml.}$$

A similar calculation reveals that if the chromate indicator of a concentration of 0.003 M is used, the volume of 0.1 M silver nitrate solution needed to make the solution saturated with respect to silver chromate is only 0.026 ml. This is hardly a significant error, whereas 0.14 ml. is.

The calculation, which the student should confirm, also shows that this excess of 0.026 ml. of 0.1 *M* silver nitrate establishes a silver ion concentration of 2.6×10^{-5} which, it will be noted, is slightly greater than that which exists at the stoichiometric point for the silver chloride equilibrium, namely 10^{-5}. Thus a slight positive titration error is inevitable in the Mohr method; that is to say, the volume of the standard silver nitrate solution necessary for the end point must be slightly greater than that corresponding to the stoichiometric point. Exactly how much greater is computed as follows for the example cited: At the end point (where silver chromate begins to precipitate) $[Ag^+] = 2.6 \times 10^{-5}$ moles per liter. At the silver chloride stoichiometric point $[Ag^+] \cong 10^{-5}$ moles per liter. The difference, 1.6×10^{-5} moles per liter, or 1.6×10^{-6} moles per 100 ml., represents the titration error. Since 1000 ml. (of 0.1 *M* silver nitrate) contains 0.1 mole, then 0.016 ml. contains 1.6×10^{-6} moles. The titration error, then, is $0.016 \cong 0.02$ ml. of silver nitrate solution. Of course the titration error is eliminated in practice if the silver nitrate solution is standardized under conditions identical with those of the analysis.

Because the concentration of the chromate indicator ion plays such an important role in the titration error, the acidity of the solution being titrated must be carefully regulated. The ionization constant of chromic acid is quite small; furthermore, in the slightly acidified solution the chromium will exist largely as the dichromate ion. For this reason a pH lower than 6 is unsuitable; and a pH greater than 10 causes the precipitation of silver oxide. The custom therefore is to adjust the pH of the titrated solution of chloride between these values.

DETERMINATION OF CHLORIDE BY MOHR METHOD

Procedure. Preparation and Standardization of Silver Nitrate Solution. Weigh out approximately 8.5 g. of pure silver nitrate and dissolve in 500 ml. of chloride-free water. (See second paragraph under Notes, p. 250.) Keep in a brown, glass-stoppered bottle. This solution is standardized using pure sodium chloride as the standard. Heat several grams of finely divided, pure sodium chloride in a porcelain crucible for 15 minutes at a dull red heat. Place while still warm in a glass-stoppered bottle and store at once in a desiccator. When cool, accurately weigh about 0.2 g., transfer to a 250 ml. porcelain casserole, dissolve in 50 ml. of chloride-free water and add 2 ml. of 0.1 *M* potassium chromate solution. Titrate with the silver nitrate solution. Although silver chromate is red, and although as the end point is approached there will be a momentary flash of red color which disappears, the end point is not marked by a true red color. Up to the end point the white precipitate of silver chloride and the yellow solution of potassium chromate combine to give a bright lemon-peel color. But at the end point the presence of a slight

precipitate of red silver chromate blends with the yellow to give a rather muddy yellow color. This is the end point. From the volume of silver nitrate solution and the weight of sodium chloride calculate the normality of the solution, using equation (1), p. 81, as usual. Duplicate determinations should agree within 1 part per 1000.

Procedure for Analysis. Accurately weigh about 0.2 g. samples of the chloride unknown, transfer to 250 ml. porcelain casserole, dissolve in 50 ml. of chloride-free water and titrate with the standard silver nitrate solution exactly as in the standardization procedure, but only after testing for acidity. To do this take a small amount of the material and dissolve in half a test tube of water. If litmus shows the solution to be acid, add 0.1 *N* sodium hydroxide to the solution in the casserole to the phenolphthalein color change; then add a drop or two of very dilute nitric acid to destroy the red color. If the test shows that the sample gives an alkaline solution, add very dilute nitric acid to the solution in the casserole until the red color of phenolphthalein barely turns colorless. Calculate the percentage of chloride in the sample. The deviation from the mean for duplicate determinations should not exceed 1 part per 1000.

Notes. The Mohr method can be applied to the determination of bromide, in the absence of chloride. Neither of these anions can be determined in the presence of other anions, such as phosphate or sulfide, which form insoluble silver salts in neutral solution. The method cannot be used in the determination of iodide or thiocyanate because the end point is not sharp, due to adsorptive properties of the precipitate.

Problem. 32.10 ml. of a silver nitrate solution is required in the titration of 0.1752 g. of pure sodium chloride. Calculate the normality of the solution. What is the "sodium chloride value" of the solution—i.e., the weight of sodium chloride equivalent to 1 ml. of the solution?

Solution. From equation (1), p. 81, we have

$$N = \frac{(1000)(0.1752)}{(32.10)(58.45)} = 0.0934$$

$$\text{NaCl value} = \frac{(0.0934)(58.45)}{1000} = 0.005458$$

Problem. A chloride unknown weighing 0.2012 g. is titrated by the Mohr method, 25.50 ml. of 0.0934 *N* silver nitrate solution being required. Calculate the percentage chloride in the sample in terms of sodium chloride.

Solution.
$$\% \text{ NaCl} = \frac{(25.50)(0.005458)(100)}{0.2012} = 69.2$$

Turbidity as a Means of Detecting End Point

The examples of this type of titration are relatively few; the Liebig method for cyanides is an important example. The method involves the formation of a soluble and stable complex as the standard solution reacts

with the unknown; after the stoichiometric point is reached there is a sudden increase in the concentration of the ion being added from the buret, and this leads to the formation of the difficultly soluble substance which causes the turbidity. To illustrate: when a cyanide solution is titrated with silver nitrate the reaction up to the stoichiometric point is

$$2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$$

but with a slight excess of silver ion a precipitate (turbidity) results due to the reaction

$$Ag(CN)_2^- + Ag^+ \rightarrow Ag\,[Ag(CN)_2]$$

(Review these equilibria as given under Complex Ions and Solubility, p. 231.) Obviously the titration error will be positive since the eye may fail to detect the first faint turbidity. However, a negative titration error is possible if, due to insufficient stirring during the titration, the silver ion concentration becomes locally so great as to form some precipitate before the stoichiometric point is actually reached. The end point is more readily detected by adding to the cyanide solution before starting the titration some ammonium hydroxide and a small quantity of potassium iodide. Under these conditions the silver argenticyanide does not precipitate after the stoichiometric point has been reached due to the formation of the silver ammonia complex, $Ag(NH_3)_2^+$, but, instead, a turbidity results because of the precipitation of silver iodide:

$$Ag(NH_3)_2^+ + I^- \rightarrow AgI + 2NH_3$$

In working with cyanides *their great toxicity should be kept constantly in mind.* Not only should the hands be washed thoroughly after handling cyanides, but one should avoid carelessly pouring cyanides into the sink without flushing down the drain. Any acid which might be in the sink would react with the cyanide to liberate the extremely poisonous hydrogen cyanide gas.

DETERMINATION OF CYANIDE BY LIEBIG METHOD

Procedure. Accurately weigh samples of about 0.3 to 0.5 g. and transfer to 250 ml. Erlenmeyer flasks. Dissolve in 25 ml. of water, add 5 ml. of concentrated ammonium hydroxide and 0.1 to 0.2 g. of potassium iodide. Dilute to 100 ml. and titrate with approximately 0.1 *M* silver nitrate solution. Calculate the percentage of cyanide in the sample. Duplicate determinations should show a deviation from the mean under 2 parts per 1000.

Problem. A cyanide sample weighing 0.5206 g. is titrated with a 0.1000 *M* silver nitrate solution, 25.08 ml. being required. Calculate the percentage of cyanide present in terms of sodium cyanide.

Solution. The normality of the silver nitrate solution must be regarded as twice as great when reacting with cyanide as when reacting with chloride because one silver ion reacts with two cyanide ions but with only one chloride ion. Therefore this silver nitrate solution must be regarded as being 0.2000 *N* for the problem at hand. The "sodium cyanide value" of the solution (i.e., the weight in grams of sodium cyanide equivalent to 1 ml. of the silver nitrate solution) is, therefore,

$$\text{NaCN value} = \frac{(0.2000)(49.02)}{1000} = 0.009804$$

Therefore

$$\% \text{ NaCN} = \frac{(25.08)(0.009804)(100)}{0.5206} = 47.2$$

Soluble Colored Compound Indicating End Point

The Volhard method for chlorides is the most common example of a precipitation titration in which a colored soluble substance, formed when the stoichiometric point is reached, marks the end point. The method is satisfactory also for the determination of bromide or iodide. In the analysis for the halides an indirect approach is employed in the sense that an amount of standard silver nitrate solution in excess of that required by the halide is added, and the excess of silver ion is determined by titrating with a standard thiocyanate solution. Silver may be determined also by this method but a direct titration of the unknown silver solution is made with a standard thiocyanate solution. (This is the procedure in standardizing the latter solution.) In either the direct or the indirect approach the reactions which take place, in order, are

$$Ag^+ + SCN^- \rightarrow AgSCN \text{ (white)}$$

and

$$Fe^{+++} + 6SCN^- \rightarrow Fe(SCN)_6^{\equiv} \text{ (red)}$$

The latter reaction is that of the indicator which is added to the solution being titrated in the form of ferric ammonium sulfate. The white silver thiocyanate precipitates and when the stoichiometric point of this reaction has been reached the next drop of thiocyanate solution brings about the formation of the red ferric thiocyanate complex ion.

The titration is carried out in nitric acid solution in contrast to other volumetric methods for silver or halide determinations which require a neutral solution. The metals of group 2 cause no serious trouble and, in the presence of nitric acid, such anions as carbonates, oxalates and phosphates, which would precipitate as the silver salts in neutral solution, do not interfere.

In the analysis of a chloride it is necessary to filter off the silver chloride which is precipitated after the addition of excess standard silver nitrate solution. This is due to the fact that if the solution is titrated

with standard thiocyanate without first being filtered, the thiocyanate will react not only with the excess silver ion which was added, but, in addition, with some of the silver chloride. In analyses for bromide or iodide, on the contrary, the silver halide need not be filtered off because silver bromide and silver iodide are so very insoluble that no appreciable reaction takes place between these precipitates and the thiocyanate solution.

DETERMINATION OF CHLORIDE BY VOLHARD METHOD

Procedure. Preparation and Standardization of Solutions. Prepare an approximately 0.1 *M* solution of silver nitrate following the instructions given under the Mohr method, p. 283. Prepare a solution of approximately 0.1 *M* potassium thiocyanate by weighing roughly 9.7 g. of the salt and dissolving in a liter of water; store in a glass-stoppered bottle. Prepare the indicator solution by saturating 100 ml. of 1 *N* nitric acid with ferric ammonium sulfate.

Determine the relative concentrations of the two standard solutions as follows: Fill a buret with the silver nitrate solution and run some 40 ml. into a 250 ml. Erlenmeyer flask. Read the buret. Add 5 ml. of 1:1 nitric acid which has been freshly boiled and cooled, and 1 ml. of indicator solution. From a second buret filled with the thiocyanate solution titrate until a reddish brown color is obtained. Approach the end point slowly and with vigorous agitation between the dropwise additions from the buret. From the buret readings calculate how many milliliters of silver nitrate solution are equivalent to 1.000 ml. of the thiocyanate solution.

Standardize the thiocyanate solution in the following manner: Accurately weigh approximately 0.2 g. samples of pure, dry sodium chloride, transfer to 250 ml. Erlenmeyer flasks and dissolve in 50 ml. of chloride-free water. Add 5 ml. of 1:1 nitric acid and then add from a buret the silver nitrate solution already prepared until a definite excess of 5 ml. or more is present. (When an excess has been added the precipitate of silver chloride will coagulate and settle quickly. Allow to settle, then add more silver nitrate from the buret; if no further precipitation takes place in the supernatant liquid an excess is assured.) Filter through a Gooch crucible and wash well. To the filtrate and washings add 1 ml. of the indicator solution and titrate with the thiocyanate solution to the reddish brown color. Knowing the relative strengths of the silver nitrate and thiocyanate solutions, calculate the volume of silver nitrate which was added in excess (i.e., that which did not react with the chloride). Subtract this volume from the total volume of silver nitrate originally added. The difference is the volume of silver nitrate equivalent to the sodium chloride; from this calculate the normality of the silver nitrate solution.

The deviation from the mean for duplicate determinations should not exceed 1 part per 1000.

Problem. A sample of 0.1302 g. of pure, dry sodium chloride is dissolved and 24.82 ml. of 0.1000 *N* silver nitrate solution is added. The solution then is titrated with potassium thiocyanate solution, of which 1.000 ml. is equivalent to 1.092 ml. of the silver nitrate solution. The titration requires 3.33 ml. of thiocyanate solution. Calculate the normality of the silver nitrate solution.

Solution. Since 1.000 ml. of thiocyanate solution is equivalent to 1.092 ml. of silver nitrate solution, 3.33 ml. of the former is equivalent to 3.64 ml. of the latter. Therefore 24.82 − 3.64 = 21.18 ml. is the volume of silver nitrate which reacted with the 0.1302 g. of the standard, NaCl. Then from equation (1), p. 81,

$$N = \frac{(1000)(0.1302)}{(21.18)(58.45)} = 0.1052$$

Procedure for Analysis. Accurately weigh samples of a soluble chloride amounting to about 0.2 g. Transfer to Erlenmeyer flasks and proceed with the analysis following the directions given just above for the standardization of the silver nitrate solution by the Volhard method. Since the normality of the silver nitrate solution is known, the percentage of chloride in the sample may be calculated. The deviation from the mean should be 1 part per 1000 or less.

End Point by Use of Adsorption Indicators

The dispersed phase of a colloidal system, because of the large surface area, usually shows a high adsorptive power. Thus, if a chemical reaction occurs in which an insoluble compound which partly assumes a colloidal state is formed, the particles are found to adsorb ions from the solution which constitutes the dispersion medium. The ion which is adsorbed is that ion of the precipitate itself which is the more abundant in the solution. A colloidal dispersion of silver chloride, for example, will adsorb either silver ions or chloride ions, depending upon which of the two is present in greater concentration in the solution. After a layer of ions has been adsorbed by the colloidal particle there follows a secondary adsorption consisting of a layer of ions of the opposite charge to that of the primary layer.

This, in brief, is the theory which forms the basis of adsorption indicators for detecting the end point in certain precipitation titrations. Of the two ions which form the precipitate there obviously will be in the surrounding solution an excess of one of them up to the stoichiometric point, but an excess of the other afterward. For example, if a chloride solution is titrated with silver nitrate solution, silver chloride precipitates (and some silver chloride is colloidally dispersed) as fast as silver ion is added from the buret; thus the chloride ion concentration exceeds that of the silver ion up to the stoichiometric point. It follows that under

these conditions the ion primarily adsorbed will be the chloride ion and the secondary layer will consist of any positive ion present, e.g., sodium. As the stoichiometric point is approached the concentration of the chloride ion in solution becomes progressively smaller; at the stoichiometric point the concentrations of the chloride ion and the silver ion become equal. Immediately past the stoichiometric point the silver ion predominates and therefore the colloidal particles now suddenly adsorb silver ions as the primary layer.

Since the adsorbent has the tendency preferentially to adsorb one of its own ions from the surrounding solution as a primary layer, an organic dye like fluorescein may be added to the solution without the adsorption of the negative ion of fluorescein. Therefore when a chloride solution which also contains this indicator is titrated with silver ion, the precipitated silver chloride remains white up to the stoichiometric point. Just past the stoichiometric point the silver ion is primarily adsorbed; thus now the secondarily adsorbed layer must be of a negative sign and the negative ion of fluorescein is adsorbed as the secondary layer. Moreover, the dye which, in solution, had a greenish yellow color, shows a pink color when adsorbed by the silver chloride particles. The change of the white silver chloride to a precipitate superficially pink in color thus marks the end point in the titration.

To summarize: up to the stoichiometric point silver chloride particles primarily adsorb chloride ions in preference to the negative ion of fluorescein; the secondary layer consists of some positive ion of the solution. The precipitate has its normal white color. With the addition of a slight excess of silver ions the particles primarily adsorb silver ions and the particles become positively charged. By secondary adsorption they then attract the negative fluorescein ions which cause the pink coloring.

In general adsorption indicators may be successfully employed only if certain conditions are fulfilled. The precipitate which is formed must be partly dispersed as colloidal particles so that the adsorptive forces will be great. If the tendency of the precipitate toward coagulation is too great (as happens in the presence of large amounts of neutral salts) it may be necessary to employ a protective colloid—e.g., dextrin—to maintain the dispersion. The indicator ion must bear a charge of the same sign as that of the titrated ion, and (a) it must not be preferentially adsorbed as a primary layer before the stoichiometric point is reached, but (b) it must be preferentially adsorbed (i.e., rather than any other ion of the same sign—like the nitrate ion in the chloride-silver titration) as a secondary layer immediately after the stoichiometric point is reached.

It must be noted that fluorescein is a very weak acid, and since the color change is due to the adsorption of its negative ion, it follows that anything which renders the concentration of that ion negligibly small

will impair or even destroy its capacity as an adsorption indicator. The hydrogen ion concentration therefore must be low; in a solution having a pH of 7 to 10 fluorescein functions very well. Eosin and dichlorofluorescein are stronger acids than fluorescein and may be used in acid solutions. However, the former cannot be used in the titration of chlorides by silver ion because its negative ion is so strongly adsorbed that the primary layer formed during the approach to the stoichiometric point does not consist exclusively of chloride ions. Thus a reddish color begins to appear before the stoichiometric point is reached.

For the application of other dyes as adsorption indicators see Kolthoff and Stenger, *Volumetric Analysis*, Vol. II, Interscience Publishers, New York, 1947.

DETERMINATION OF CHLORIDE BY ADSORPTION INDICATOR METHOD

Procedure for Standardization. Prepare a solution of silver nitrate about 0.1 *M* in the manner given for the Mohr method for determining chlorides. Accurately weigh samples of the standard, sodium chloride, which has been heat-treated as described under the Mohr method, of about 0.2 g. each, transfer to 250 ml. Erlenmeyer flasks and dissolve in about 50 ml. of chloride-free water. Prepare the indicator solution by dissolving 0.1 g. of fluorescein in 100 ml. of 70 per cent alcohol or 0.1 g. of sodium fluoresceinate in 100 ml. of water. Or dissolve 0.1 g. of dichlorofluorescein in 100 ml. of 70 per cent alcohol or 0.1 g. of its sodium salt in 100 ml. of water. Add 10 or 12 drops of either indicator to the sodium chloride solution and 0.1 g. of dextrin. Titrate, with continuous agitation, with the silver nitrate solution. Keep away from direct sunlight. The end point has been reached when the white precipitate suddenly takes on a reddish tinge. From the volume of silver nitrate solution used and the weight of the standard employed, calculate the normality of the solution and its chloride value. Duplicate results should not deviate from the mean by more than 1 part per 1000.

Procedure for Chloride Analysis. Accurately weigh out samples of 0.2 g. or slightly more of the dried material for analysis. Transfer to 250 ml. Erlenmeyer flasks, dissolve in about 50 ml. of chloride-free water and proceed according to the above directions for the standardization. From the normality or the chloride value of the silver nitrate solution and the volume used for the titration, calculate the percentage of chloride in the sample. Duplicate determinations should show a deviation from the mean not exceeding 1 part per 1000 for samples of fairly high chloride content.

Notes. Dextrin retards the coagulation of silver chloride and thus maintains the adsorptive property of the particles.

The above method may be applied to the titration of bromides, iodides and thiocyanates as well as chlorides. Eosin may be used as the indicator in the analysis of iodides or thiocyanates if the pH of the solution is greater than 3.

Spot Test Indicators. In certain titrations for which no internal indicator has been discovered a drop of the titrated solution is removed as the stoichiometric point is approached. This drop is tested on a porcelain spot-plate with a drop of a reagent which will reveal the presence of the titrated substance or of the titrating solution. The end point for the titration has been reached when a spot test shows the absence of the constituent being titrated. For an example of this method of determining the end point see pp. 202 and 203.

Questions and Problems

1. Show by calculations that 2 ml. of 0.1 *M* potassium chromate solution will establish a suitable concentration of chromate indicator ion in a Mohr titration if the final volume is about 75 ml.
2. Explain why, in the determination of chloride by the Mohr method, the pH of the solution should be adjusted to a value between 7 and 10.
3. Hydrochloric acid is, of course, a strong acid. Would it be possible, nevertheless, to standardize a hydrochloric acid solution by a Mohr titration? Explain.
4. Calculate the titration error when 50 ml. of an approximately 0.1 *N* solution of a chloride is titrated with 0.1 *N* silver nitrate solution, using 10^{-5} *M* potassium chromate as the indicator.
5. If *M* represents the molarity and *N* the normality of a silver nitrate solution explain why $M = N$ when the solution is used in a Mohr titration, whereas $2M = N$ when the solution is used in a cyanide determination by the Liebig method.
6. In the Volhard method why must the precipitate of silver chloride be filtered before the solution may be titrated with standard thiocyanate solution, whereas silver bromide or silver iodide need not be filtered off before the titration?
7. In the chloride determination by the adsorption indicator method using fluorescein as the indicator, why must the pH of the solution be above 7? Why below 10? Why may dichlorofluorescein be used in an acid solution of a chloride? Why is eosin not suitable as an adsorption indicator in a chloride determination?
8. What is the molarity of a silver nitrate solution if 33.86 ml. of it is required to titrate a 0.4902 g. sample of pure, dry potassium cyanide?
   Answer: 0.1112 *M*.
9. A cyanide sample weighing 0.5100 g. is titrated with 0.1010 *M* silver nitrate solution, 24.48 ml. being required. Calculate the percentage of cyanide present in terms of sodium cyanide.
   Answer: 47.5%.
10. A silver nitrate solution is available 1.000 ml. of which is equivalent to 0.007508 g. of potassium chloride. A 0.2452 g. sample of a chloride is analyzed

by the Volhard method. A volume of 28.00 ml. of the silver nitrate solution is added and the solution is titrated with a potassium thiocyanate solution 1.000 ml. of which is equivalent to 1.046 ml. of the silver nitrate solution. The titration requires 5.15 ml. of thiocyanate solution. Calculate the percentage of chloride in the sample.

Answer: 32.9%.

Chapter 17

POTENTIOMETRIC TITRATIONS[1]

It has been mentioned already in Chapter 10 that, inasmuch as it is possible to calculate the e.m.f. developed at the stoichiometric point by a given cell, the end point for a titration may be detected without the use of color indicators. It is only necessary that the e.m.f. at the stoichiometric point be computed and the titration carried out until this e.m.f. is registered. It is common practice to make numerous readings of the e.m.f. of the cell during a titration and to carry the titration somewhat beyond the stoichiometric point. Since the e.m.f. varies sharply in the vicinity of the stoichiometric point, it is not necessary to take many readings until near this point, but here the recordings should be made after the addition of each drop from the buret. After the data have been secured a graph may be constructed, plotting the e.m.f. as the ordinate against volume of reagent added as the abscissa. A perpendicular dropped from the steepest portion of the curve will indicate the volume of reagent necessary for the titration.

The Potentiometer. Potentiometric titrations are carried out by use of the instrument called the potentiometer. Fig. 37 illustrates a simple type of potentiometer connected to the indicator electrode (in the solution to be titrated) and a reference, calomel electrode. The purpose is to measure the e.m.f. of the cell during the course of the titration. This cannot be done with an ordinary voltmeter since the current necessary to deflect the pointer, coming as it does from the cell, causes changes in concentration within the cell, thereby diminishing the e.m.f. even while the measurement is being made. To circumvent this situation the e.m.f. of the cell, E_x in the figure, is balanced with an opposing e.m.f. from B_a so that no current flows from the cell.

A wire BA of uniform resistance is connected by heavy copper wire of no appreciable resistance to battery B_a which usually is a lead storage battery but may be two dry cells. E_x is the cell the e.m.f. of which is to be measured. It is connected, on the one side, through galvanometer G, to the resistance wire at terminal B, the zero point of resistance. On the other side E_x is connected, through tapping key K, to sliding contact C which may be moved along BA to such a position that the key may be

[1] For a review with a bibliography see Furman, *J. Ind. Eng. Chem., Anal. Ed.*, **14**, 367 (1942).

tapped without causing any deflection of the galvanometer. The galvanometer thus functions as a nullpoint instrument. When this condition prevails the e.m.f. from B_a is just balanced by the opposing (note the two polarities) e.m.f. from E_x. The ratio of the two electromotive forces must now be equal to the ratio of the corresponding resistances, or $E_x:B_a = BC:BA$, and, since the resistances are directly proportional to the lengths of the resistance wire involved, it follows that $E_x:B_a =$ (length of BC):(length of BA). Of these four terms B_a and the length BA are known, and the length BC is measured; thus E_x is readily calculable.

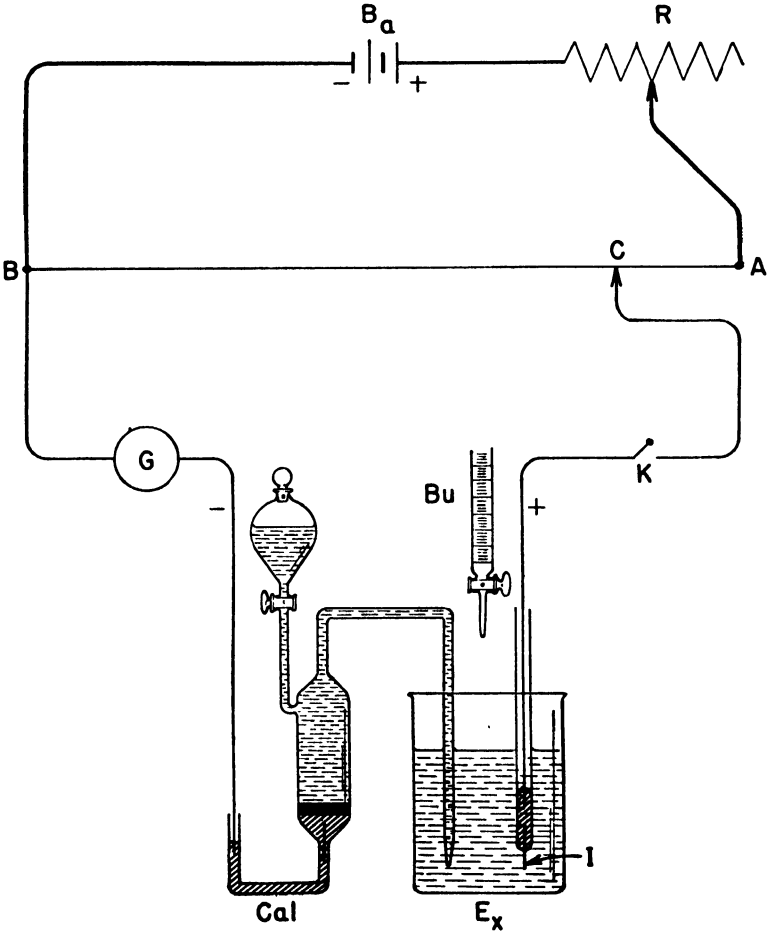


FIG. 37. Principle of the potentiometer as used in potentiometric titrations. (B_a) Battery. (R) Variable resistance. (BA) Slide wire. (C) Sliding contact. (K) Tapping key. (I) Indicator electrode. (Cal) Calomel electrode. (G) Galvanometer. (Bu) Buret. (E_x) The cell the e.m.f. of which is to be measured.

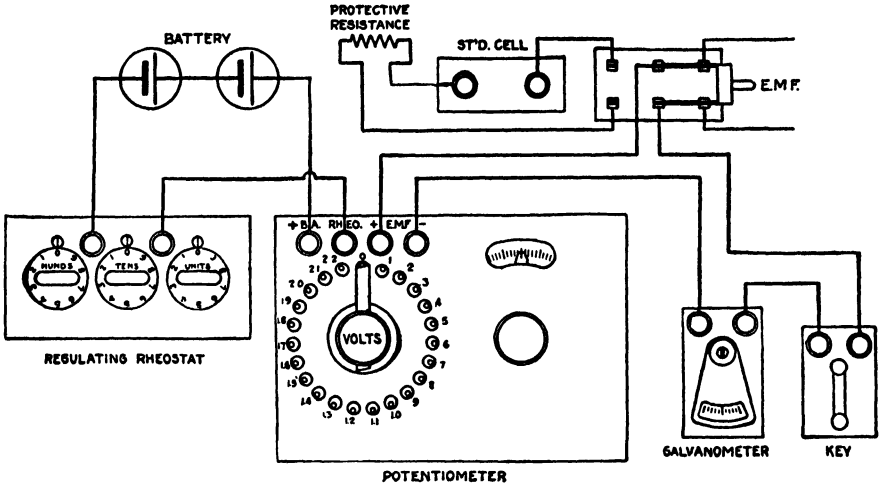


FIG. 38. Apparatus for precise potentiometric titrations. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

The e.m.f. from B_a is made known by replacing E_x of Fig. 37 (e.m.f. of Fig. 38) with a standard cell which provides an accurately known e.m.f. The Weston cell with an e.m.f. at 20° of 1.0183 volts is commonly employed for this purpose. The e.m.f. from B_a may be regulated to any desired value by means of the rheostat R.

In potentiometric titrations the absolute values of E_x are not necessary; it is sufficient to read the changes in BC, particularly in the neighborhood of the stoichiometric point, from the instrument. Since BA is constant, E_x is directly proportional to BC and therefore the readings of BC indicate the change of potential in the cell, E_x.

TITRATIONS OF ACIDS AND BASES

The Hydrogen Electrode. Obviously potentiometric titrations may be made in the titration of acids and bases provided a relation exists between the hydrogen ion concentration and the electrode potential of a given electrode immersed in the solution being titrated. The hydrogen electrode may be so used. If the hydrogen electrode dips into the unknown solution and is connected to another half-cell, for example to a calomel half-cell as shown in Fig. 39, an electric current will flow in the external circuit. An instrument for measuring the e.m.f. must, of course, be inserted in the external circuit. This cell may be represented

$$\begin{matrix} \text{Hg} \\ \text{Hg}_2\text{Cl}_2 \end{matrix} \Big| \text{KCl (1 } M\text{)} \Big\| \begin{matrix} \text{H}^+ \text{ (X } M\text{)} \\ \text{H}_2 \text{ (1 atm.)} \end{matrix} \Big| \text{Pt}$$

From Table 17 we have

$$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-, \quad E^0_{Cal} = 0.28$$
$$2H^+ + 2e = H_2, \quad E^0_H = 0.00$$

so that the e.m.f. of the cell, E_c, $= E_1 - E_2$ or

$$E_c = E^0_{Cal} - E^0_H - 0.0591 \log [H^+]$$
$$= 0.28 - 0.00 - 0.0591 \log [H^+]$$
$$E_c = 0.28 - 0.0591 \log [H^+] \quad (1)$$

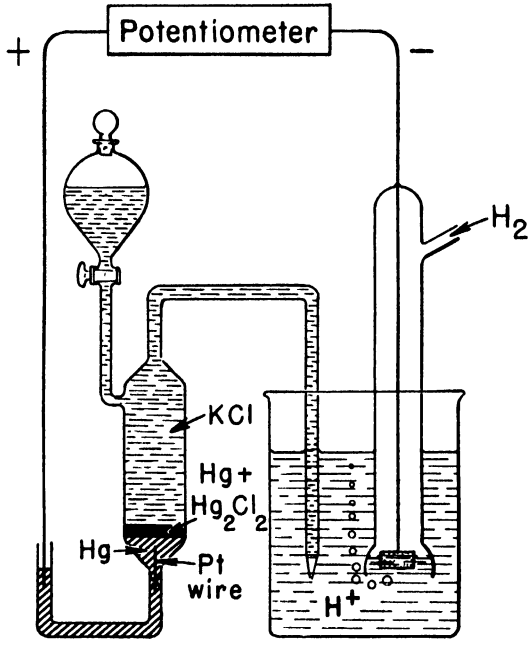


FIG. 39. Calomel and hydrogen electrodes for a potentiometric titration.

Since pH $= -\log [H^+]$ we may substitute in equation (1) and obtain

$$E_c = 0.28 + 0.0591 \text{ pH}$$

from whence

$$\text{pH} = \frac{E_c - 0.28}{0.0591} \quad (2)$$

The hydrogen electrode is subject to poisoning and, even with great care in handling it, erroneous readings may be obtained or the circuit actually may go dead. As a result it is usual to employ some other electrode the potential of which also is proportional to the hydrogen ion concentration. One of the most commonly used is the glass electrode.

The Glass Electrode.[2] The glass electrode consists of a glass tube terminating in a thin glass bulb containing a solution of hydrochloric acid, 0.1 *N* or less. An electrode extends through the tube and dips into this solution. The electrode must have a constant potential in regard to the hydrochloric acid solution. It may be a silver electrode coated with silver chloride or it may be a platinum electrode; if the latter, then some quinhydrone (see next section) is added to the solution, making it a quinhydrone electrode. The glass bulb is placed in the solution the pH of which is to be determined. The bulb acts as a membrane which would seem to be permeable to hydrogen ions. If a calomel electrode also is placed in the unknown solution the e.m.f. between the calomel and the glass electrodes may be measured. The cell may be represented thus:

$$\begin{matrix}\text{Ag}\\ \text{AgCl}\end{matrix}\Big|\ \text{HCl (0.1 } M\text{)}\ \Big|\ \text{Glass}\ \Big|\ \begin{matrix}\text{Solution being}\\ \text{analyzed}\end{matrix}\ \Big\|\ \text{KCl (1 } M\text{)}\ \Big|\ \begin{matrix}\text{Hg}\\ \text{Hg}_2\text{Cl}_2\end{matrix}$$

(Reference electrode)

The e.m.f. established may be evaluated by the methods already outlined. It is necessary, of course, in order to use the glass electrode to determine hydrogen ion concentration, to know the value of E^0_g. Due to difference in action of the glass surfaces in glass electrodes, one usually encounters small differences of potential of the order of a few millivolts. This effect, particularly noticeable with new electrodes, is known as the asymmetry potential, and it cannot be predicted. However, the value of E^0_g may be obtained easily by placing the glass electrode and a hydrogen electrode in an acid solution of any concentration. The e.m.f. which is registered is evidently the E^0_g value of the particular glass electrode.

Because of rather high resistance of the glass membrane it is necessary to use a vacuum-tube amplifier circuit instead of the usual galvanometer in connection with the glass electrode. In solutions of pH values greater than 9 the glass electrode gives unduly high potentials which cause a negative error in determining pH. This is probably due to the diffusion of other ions through the glass membrane when the hydrogen ion concentration is low. If a thinner glass electrode is employed the resistance will be lower, but then the bulb is rather fragile.

Advantages of the glass electrode are that the e.m.f. is independent of the presence of oxidizing or reducing agents and of poisons; it may be used in unbuffered solutions; rapid determinations of pH may be made because constant readings are obtained immediately; and, since it may be constructed in very small size, it can be used to measure the pH of very small samples. It is the most nearly universally adaptable electrode

[2] Dole, *Principles of Experimental Electrochemistry*, The McGraw-Hill Book Co., New York, 1935; *The Glass Electrode*, John Wiley and Sons, New York, 1941; *J. Am. Chem. Soc.*, **53**, 4260 (1931); *ibid.*, **54**, 3095 (1932).

so far devised for pH measurements. Many instruments are on the market which give in one compact case a glass electrode, a saturated calomel electrode, a vacuum-tube potentiometer and a standard cell. The instrument gives pH readings directly without any calculations on the part of the operator. These pH meters may be adjusted for temperatures other than 25° and also for variations of E^0_g. The latter adjustment is made by placing a buffer solution of known pH in the cell vessel and setting the dial at this known pH, after which an adjusting knob is turned until the galvanometer is at zero. The most important use of the glass electrode is in the determination of pH rather than in electrometric titrations.

The Quinhydrone Electrode. Quinhydrone is an organic, equimolar compound of quinone and hydroquinone. It dissolves sparingly in water and is partly dissociated into quinone and hydroquinone.

$$\underset{\text{Quinhydrone}}{C_6H_4O_2.H_2C_6H_4O_2} \rightleftarrows \underset{\text{Quinone}}{C_6H_4O_2} + \underset{\text{Hydroquinone}}{H_2C_6H_4O_2}$$

Or, if we let Q stand for $C_6H_4O_2$, the equation becomes

$$Q.H_2Q \rightleftarrows Q + QH_2$$

To measure the pH of a solution with the quinhydrone electrode it is only necessary to add some quinhydrone to the unknown solution and immerse a platinum electrode and a reference electrode such as a calomel electrode. The cell is represented by

$$Pt \left| Q,\ QH_2,\ H^+(X\ M) \right\| KCl\ (1\ M) \left| \begin{matrix} Hg \\ Hg_2Cl_2 \end{matrix} \right.$$

The quinone and hydroquinone represent an oxidation-reduction system,

$$Q + 2H^+ + 2e \rightleftarrows QH_2$$

and in a solution saturated with quinhydrone the concentrations of Q and QH_2 are equal, for a molecule of the quinhydrone yields one each of the two latter. Thus the e.m.f. of a cell embodying the quinhydrone electrode will vary directly with the hydrogen ion concentration. This may be seen from the equations

$$\begin{aligned} Q + 2H^+ + 2e &= QH_2, & E^0_Q &= 0.70 \\ Hg_2Cl_2 + 2e &= 2Hg + 2Cl^-, & E^0_{Cal} &= 0.28 \\ \hline Q + 2H^+ + 2Hg + 2Cl^- &= QH_2 + Hg_2Cl_2, & E^0_Q - E^0_{Cal} &= 0.42 \end{aligned}$$

Thus

$$E_c = E_1 - E_2 = 0.42 - \frac{0.0591}{2} \log \frac{[QH_2][Hg_2Cl_2]}{[Q][Hg]^2[Cl^-]^2[H^+]^2}$$

In the logarithmic term all of the components are at standard state except Q and QH_2, which are equal (their ratio is therefore unity), and

hydrogen ion. Therefore

$$E_c = 0.42 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$= 0.42 - 0.0591 \log \frac{1}{[H^+]}$$

$$E_c = 0.42 - 0.0591 \text{ pH}$$

So that

$$\text{pH} = \frac{0.42 - E_c}{0.0591} \tag{3}$$

The quinhydrone electrode comes quickly to equilibrium, is not easily poisoned, avoids the use of hydrogen gas which is necessary with the hydrogen electrode, and is experimentally simple to use. This electrode has, however, important limitations. It is not accurate at pH values above 9. At this and higher pH values hydroquinone, a weak acid, becomes appreciably ionized and thus changes the pH of the solution being analyzed. This also alters the Q/QH_2 ratio, a result produced furthermore by the presence of either oxidizing agents or reducing agents; any change in the Q/QH_2 ratio from unity invalidates equation (3) above. Furthermore, the presence of high concentrations of salts slightly affects the potential. In the absence of these disadvantageous conditions the quinhydrone electrode is highly valuable as a means of measuring pH. Note that if E_c in equation (3) is assigned a value of zero, and we solve for pH, a value of 7.1 is obtained. This means that at pH values above 7.1 the e.m.f. of the cell becomes negative and the calomel electrode then is the positive electrode.

Potentiometric Oxidation-Reduction Titrations

It has been pointed out already (p. 176) that the potential of an electrode of a noble metal like platinum immersed in a solution of a substance present in both its higher and lower valence states is given the expression

$$E = E^0 + \frac{0.0591}{n} \log \frac{[\text{H.V.S.}]}{[\text{L.V.S.}]}$$

As one carries out the titration of ferrous iron, for example, there must result a continuous change in the ratio [H.V.S.]/[L.V.S.] accompanied by a corresponding change in the value of E. By using the platinum electrode in such a solution, along with a reference electrode such as the calomel electrode, the value of E_c, the e.m.f. of the resulting cell, will vary continuously. By measuring E_c during the course of the titration and plotting these e.m.f. values as the ordinate against volume added from the buret as the abscissa, the end point of the titration may be obtained.

Potentiometric Precipitation Titrations

If a metallic electrode dips into a solution of its ions the electrode potential will vary with a change in concentration of that ion; thus if a titration involves the precipitation of this ion the potential will serve as a measure of the diminishing concentration of the ion during the titration. For example, consider the precipitation of silver chloride during the titration of chloride ion by silver ion. The unknown ion may be determined if a reference electrode such as the calomel electrode is used with a silver indicator electrode. The cell is

$$\begin{matrix}\text{Ag}\\ \text{Ag}^+\ (\text{X}\ M)\end{matrix}\ \Big\|\ \text{KNO}_3\ \Big\|\ \text{KCl}\ (1\ M)\ \Big|\ \begin{matrix}\text{Hg}\\ \text{Hg}_2\text{Cl}_2\end{matrix}$$

where the KNO_3 is simply a salt bridge. (The KCl of the calomel electrode is not in direct contact with the titrated solution.) The e.m.f. of the cell will change as silver chloride is precipitated and is calculated thus:

$$\begin{aligned} E_c = E_1 - E_2 &= E^0_{Ag} + 0.0591 \log [Ag^+] - E^0_{Cal} \\ &= 0.80 - 0.28 + 0.0591 \log [Ag^+] \\ E_c &= 0.52 + 0.0591 \log [Ag^+] \end{aligned}$$

When the stoichiometric point is reached there occurs, of course, a sudden change in the concentration of silver ion and therefore an abrupt change in the e.m.f. of the cell. If the e.m.f. of the cell is plotted against volume of solution added from the buret, the end point is found as usual by dropping a perpendicular from the steepest portion of the curve to the abscissa. Thus no color indicator is needed in order to establish the end point.

To illustrate the calculation of the concentration of silver ion at a given stage in the titration, suppose that the e.m.f. of the above cell is found to be 0.22 volt. Then from the above equation

$$\begin{aligned} 0.22 &= 0.52 + 0.0591 \log [Ag^+] \\ \log [Ag^+] &= \frac{-0.30}{0.0591} = -5.08 = (-6.00 + 0.92) \\ [Ag^+] &= 8.3 \times 10^{-6} \end{aligned}$$

Potentiometric Determinations

Acid-Base Titration Using the Hydrogen Electrode. With a pipet measure a definite volume of acid the normality of which is to be determined, and place in a beaker of suitable size. Run a small amount of potassium chloride from the reserve bulb of the calomel electrode (see Fig. 39) to insure a fresh liquid junction. Place the calomel electrode and a hydrogen electrode in the acid solution and see that the hydrogen

electrode is fully submerged by adding, if necessary, a little water. Connect the calomel electrode to the positive terminal of the potentiometer (Fig. 39) and the hydrogen electrode to the negative terminal. Connect a tank of hydrogen to the hydrogen electrode after inserting in the line a wash tower containing alkaline pyrogallol (or a tube of platinized asbestos) which removes any oxygen in the gas. Turn on the hydrogen so that a stream of gas passes through the electrode and bubbles steadily out through the acid in the beaker. Place the buret containing the standard sodium hydroxide over the beaker and titrate the acid. Measure the e.m.f. at intervals throughout the titration. Only a few readings are taken at first, but as the stoichiometric point is approached readings should be made after smaller and smaller additions of base, and finally after each few hundredths ml. The e.m.f. of course changes rapidly in the vicinity of the stoichiometric point. Continue adding base until the stoichiometric point has been passed by 10 ml. or so of base. From equation (2) calculate the pH for each e.m.f. reading taken. Plot the pH (or the e.m.f.) as the ordinate against volumes added from the buret as the abscissa. From the graph determine the end point of the titration and calculate the normality of the acid. Duplicate determinations should give a relative deviation from the mean of not more than 1 part per 1000.

Acid-Base Titration Using the Quinhydrone or the Glass Electrode as the Indicator Electrode. The setup of the apparatus is similar to that described in the preceding section except that the hydrogen electrode is replaced by the quinhydrone or by the glass electrode. Judging from the electrode potential of whichever indicator electrode is chosen, decide which terminal of the potentiometer is connected to the indicator electrode and which to the calomel, reference electrode. If the quinhydrone electrode is selected place a few crystals of quinhydrone in the beaker with the acid to be titrated. Remember that when an acid is titrated using this electrode the e.m.f. decreases, so that when it becomes zero the polarity of the electrodes is switched and subsequent readings from the potentiometer are recorded as negative. Calculate the pH corresponding to each reading and plot the results as explained in the preceding section. Calculate the normality of the acid. The relative deviation from the mean should be 1 part per 1000 or lower.

Note. It is instructive to add an indicator such as methyl orange or phenolphthalein and note the pH range through which it undergoes its color change.

Determination of Normality of Ferrous Sulfate as a Reductant. Arrange the apparatus as described under acid-base titrations above, except replace the hydrogen electrode with the platinum electrode. (Retain the calomel electrode.) Place in the beaker a freshly prepared, approximately 0.1 *N* solution of ferrous sulfate and add 10 ml. of concentrated

sulfuric acid which has been diluted by pouring into 50 ml. of water. Connect the platinum electrode to the positive terminal of the potentiometer. Titrate the solution with a standard solution of permanganate, ceric or dichromate solution. Calculate the exact normality of the ferrous sulfate solution. The relative deviation from the mean should be under 2 parts per 1000.

Precipitation Titration. Determination of Chloride. The apparatus is the same as used for the acid-base titration except that a silver indicator electrode is used instead of the hydrogen electrode. The silver electrode may be a silver wire or a silver-plated platinum wire. A calomel electrode serves as the reference electrode. The data may be plotted as in the previous potentiometric experiments; that is, either the e.m.f. or the pAg ($= -\log [Ag^+]$) against volume of silver ion (standard silver nitrate solution) added from the buret. From the equation already given (p. 300),

$$E_c = 0.52 + 0.0591 \log [Ag^+]$$

it follows that

$$pAg = \frac{0.52 - E_c}{0.0591}$$

From the graph the end point of the titration is revealed and the calculation of percentage of chloride is made readily. Duplicate determinations should show a relative deviation of not over 2 parts per 1000 for samples of soluble chlorides.

Questions and Problems

(All temperatures are 25°)

1. The value of E^0_g for a glass electrode may be determined by placing the glass electrode and a hydrogen electrode in an acid solution of any concentration. The e.m.f. of the cell is the value of E^0_g. Prove this statement mathematically.
2. Calculate the pH of a solution in which a normal calomel electrode and a quinhydrone electrode establish an e.m.f. of + 0.100 volt.
   Answer: 5.4.
3. Calculate the pH of a solution in which a normal calomel electrode and a quinhydrone electrode establish an e.m.f. of zero.
   Answer: 7.1.
4. Given two HCl solutions. The more concentrated is 0.07 *M*. A hydrogen electrode is placed in each and the solutions are connected internally by a salt bridge. An e.m.f. of + 0.110 volt is read on the potentiometer. What is the pH of the more dilute solution?
   Answer: 3.1.
5. In determining the pH of a solution by means of a hydrogen indicator electrode and a normal calomel electrode the e.m.f. was found to be + 0.420 volt Calculate the pH of the solution.
   Answer: 2.4.

Chapter 18

ELECTROANALYSIS

Theory

Electrolysis is the decomposition of some component in a solution by the passage of an electrical current through the solution. In analysis by electrolysis, a constituent, usually a metal, is deposited on the electrode and from the weight of the substance deposited its percentage in the sample may be calculated. In a solution containing several ions of a given sign, say cations, it is theoretically, and often practically, possible to separate them one by one from the solution, since the cation with the highest oxidation potential (the greatest electron affinity) will be deposited at a given low applied voltage, while another cation with a lower oxidation potential will deposit only after the impressed voltage has been increased. (Restudy statements (a) (b) (c) and (d), p. 172.)

Faraday's law states that the quantities of substances liberated at the electrodes are directly proportional to the amount of electricity passing through the solution. A given amount of electricity will set free weights of different substances which are in the ratio of their equivalent weights. A gram equivalent weight of any element is set free by the passage of one faraday, i.e., 96,500 coulombs, of electricity, for example: 107.9 g. of silver, 31.77 g. of copper or 1.008 g. of hydrogen. Faraday's laws make no statement in regard to the electrical pressure, or voltage, which must be applied in order to bring about the liberation of substances at the electrodes. Let us examine this latter question.

Suppose that a 1 *M* solution of cupric chloride is electrolyzed between platinum electrodes. After the current has passed through the solution for a brief period of time, copper has been deposited at the cathode and chlorine liberated at the anode. If now for a moment we ignore the fact that current is being forced through the solution from an outside source, and view the system as a voltaic cell, we should represent that cell as

$$\mathrm{Pt} \left| \begin{matrix} \mathrm{Cl_2\ (1\ atm.)} \\ \mathrm{Cl^-\ (2\ \mathit{M})} \end{matrix} \right\| \mathrm{Cu^{++}\ (1\ \mathit{M})} \Big| \mathrm{Cu}$$

and it is obvious that such a cell would yield an e.m.f. of a calculable voltage. The calculation of this voltage is made in the manner already presented in Chapter 10 and is

$$(1) \qquad E_c = E_1 - E_2 = E^0_{Cl} - E^0_{Cu} - \frac{0.0591}{2} \log [Cu^{++}][Cl^-]^2$$

for the reactions are

$$\begin{aligned} Cl_2 + 2e &= 2Cl^-, \; E^0_{Cl} = 1.36 \\ Cu^{++} - 2e &= Cu, \; E^0_{Cu} = 0.34 \end{aligned}$$

Thus, $Cl_2 + Cu = 2Cl^- + Cu^{++}, \; E^0_{Cl} - E^0_{Cu} = 1.02$ volts

Solving for E_c we have

$$E_c = 1.02 - \frac{0.0591}{2} \log (1)(2)^2$$

$$E_c = 1.02 - 0.02 = 1.00 \text{ volt}$$

It follows that since the cell which comes into being as a result of the electrolysis of the copper chloride is capable of producing an e.m.f. of 1.00 volt in a direction counter to that being passed through the cell from the outside source, then this counter e.m.f. of 1.00 volt must at least be exceeded slightly by the impressed e.m.f. if the electrolysis is to continue. However, it is seen from equation (1) that as the concentrations of the chloride and copper ions in the solution diminish the counter e.m.f. increases, so that as the electrolysis of the solution proceeds the necessary, impressed voltage becomes greater. To illustrate: when the copper ion concentration has been decreased, through electrolysis, to a value of 0.001 mole per liter, that of the chloride ion will be 0.002. At these concentrations the counter e.m.f. becomes

$$E_c = 1.02 - \frac{0.0591}{2} \log (10^{-3})(2 \times 10^{-3})^2$$

$$E_c = 1.02 + 0.26 = 1.28 \text{ volts}$$

and at this stage of the electrolysis the e.m.f. imposed from the outside source for continuation of the electrolysis must at least be slightly greater than 1.28 volts.

Decomposition Voltage. We see from what has been said in the above section that to carry out electrolysis continuously a certain minimum e.m.f. called the theoretical *decomposition voltage* is necessary, and that as the electrolysis continues this necessary minimum becomes progressively greater. However, the voltage actually required, either at the beginning or at any stage during electrolysis, is usually greater than the calculated counter e.m.f. This actual decomposition voltage is governed not only by the counter e.m.f. but, in addition, by a slight current resistance offered by the solution, and, more important, by what is known as overvoltage. The overvoltage is that excess potential, above the theoretical decomposition voltage, necessary for the electrolysis. The mechanism of overvoltage is not completely understood. It manifests itself chiefly at electrodes where a gas may be evolved. Its magnitude in any

case depends upon several factors, among which the following may be mentioned.

1. The material and the nature of the electrodes. A difference in the degree of overvoltage is found for a given substance when the electrolysis is carried out between different electrodes. Overvoltage for hydrogen is practically zero if platinum black is the cathode but is high if the cathode is mercury. It is much higher on polished platinum than on platinum black. The latter suggests that the phenomenon may be related either to the catalyzed conversion of ions to atoms or of the atoms of the gas into the diatomic molecule.

2. The nature of the particular substance deposited or liberated. Overvoltage for metals in general is relatively small, from a few hundredths volt to several tenths volt. But for gases the overvoltage as a rule is large.

3. The temperature of the solution. At higher temperatures the extent of overvoltage is decreased, for the rate of migration of ions is accelerated and local exhaustion of the ions in the region around the electrodes is retarded. Hydrogen overvoltage, however, appears to be independent of temperature.

4. Current density. This is the quantity of electrical current per unit area of electrode surface, in amperes per square centimeter. The overvoltage increases at high current densities, and approaches a maximum at very high current density.

5. Depletion of ion concentration around the electrode. The overvoltage becomes higher as electrolysis proceeds and the concentration of the deposited ion is lessened in the immediate vicinity of the electrode. Obviously vigorous stirring of the solution will reduce this effect.

Overvoltage is of most importance from the standpoint of analytical chemistry in the cases of hydrogen and oxygen overvoltages. Usually some hydrogen is evolved at the cathode simultaneously with the deposition of the desired metal due to the depletion of the metallic ions around the electrode. This promotes the complete deposition of the metallic ions which otherwise would be difficult. The amalgamation of zinc for use in the Jones reductor prevents the evolution of hydrogen due to the high overvoltage of hydrogen on mercury.

Electrolytic Separation of Metals. The separation of a given cation in a solution containing other cations may be brought about provided the decomposition voltages of the several compounds are sufficiently divergent. As the deposition of the cation continues the decreased concentration causes a higher counter e.m.f. and a greater decomposition voltage; the impressed e.m.f. therefore must exceed slightly the decomposition voltage which prevails when the concentration of the cation being deposited is negligibly small. As a rule the decomposition voltage of any other compound present must not be exceeded or else its cation

also would be deposited. Suppose, for example, the decomposition voltage of a solution of zinc sulfate is 2.55 and of copper sulfate[1] is 1.49. If a current of 2.0 volts is passed through a solution containing both of these salts the copper may be almost totally plated out on the cathode before any zinc is deposited. If a new cathode is now placed in the solution and the potential is increased to above 2.55 volts, all of the zinc will be liberated. In this manner the rapid analysis of metals and alloys often may be made.[2]

The extent to which complete separation of metals may be effected is calculated by methods previously encountered. We might wish to know how much copper ion remains in solution in the above electrolysis when the zinc ion begins to deposit. When both ions begin to deposit there will be a condition of equilibrium between the copper and zinc ions. From the cell

$$\mathrm{Cu} \mid \mathrm{Cu^{++}} \parallel \mathrm{Zn^{++}} \mid \mathrm{Zn}$$

we know that

$$E_c = E^0_{Cu} - E^0_{Zn} - \frac{0.0591}{2} \log \frac{[Zn^{++}]}{[Cu^{++}]}$$

At equilibrium conditions $E_c = 0$ and since $E^0_{Cu} = 0.34$ and $E^0_{Zn} = -0.76$ we obtain

$$0 = 0.34 + 0.76 - \frac{0.0591}{2} \log \frac{[Zn^{++}]}{[Cu^{++}]}$$

and solving for the ratio of the concentrations,

$$\frac{[Zn^{++}]}{[Cu^{++}]} = 1.7 \times 10^{37}$$

This means that zinc ions begin to deposit only when the copper ion concentration has been reduced to a negligibly small quantity; therefore, the electrolytic separation of copper and zinc is feasible.

Effect of Acidity on Electrolyzed Solution. Since any aqueous solution contains a finite hydrogen ion concentration the possibility of the liberation of hydrogen exists in any electrolysis. When a metal is being deposited the simultaneous deposition of much hydrogen may prevent a dense plating out of the metal and this may lead to loss of some of the metal before weighing the cathode. Metals which lie below hydrogen cannot be deposited from an acidic solution unless the overvoltage of hydrogen is great. Even zinc and nickel may be deposited without resorting to highly alkaline solutions because of hydrogen overvoltage. In a manner exactly similar to the above calculation of the ratio of the copper ion–zinc ion concentrations it may be shown that if the hydrogen overvoltage is, for example, 0.6 volt, zinc ions will continue to deposit even

[1] Le Blanc, *Z. physik. Chem.*, **8**, 299 (1891); *ibid.*, **12**, 333 (1893).
[2] Smith, *Electro-Analysis*, The Blakiston Company, Philadelphia, 1918.

when $[Zn^{++}] = 10^{-5}$ if the pH is 5.2. The effect of the pH of the solution in the electrolytic separation of copper and nickel is interesting. The decomposition voltage of nickel sulfate is only about a half volt higher than that of copper sulfate, so that the separation of the metals by keeping the voltage between the two decomposition potentials would be difficult. No trouble is encountered, however, if the solution is acidified with sulfuric acid and a potential of 2 or 3 volts is applied. The copper is then deposited; but, even though the decomposition voltage of nickel is exceeded, no nickel is deposited because there is a good supply of hydrogen ion around the cathode. After the copper is deposited the solution may be made alkaline with ammonia and the electrolysis continued to plate out the nickel.

The applied voltage in any electrolysis should be as high as may safely be employed, since at low potentials the current may be so small that too long a time period will be necessary for the complete deposition.

Analysis by Electrolysis

The electrolytic deposition of a given metal from a solution containing two or more cations usually is accomplished with solutions of the nitrates or sulfates of the metals. As a rule chlorides should not be present since chlorine, when liberated, attacks the electrodes. Often solutions of salts forming complex ions bring about better metallic deposits, as in the case of silver. Furthermore, complex ion formation is a means sometimes employed to adjust one or more of the cations to suitable concentrations. Silver ion concentration will be quite different if it is in equilibrium with the complex argenticyanide ion, $Ag(CN)_2^-$, for example. If two cations form corresponding complex ions of markedly different stability the electrolytic separations of the metals may be greatly facilitated because the decomposition voltage of the two compounds will differ widely.

The majority of metals are deposited as such at the cathode during electrolysis, but some—for example, manganese and lead—are liberated at the anode as the dioxides. In order to avoid a loosely adhering deposition on the electrodes, so that washing, drying and weighing can be carried out without loss of material, it is common practice to maintain as low a current density as feasible and to avoid too rapid electrolysis. The simultaneous liberation of much hydrogen at the cathode appears to prevent a compact metallic deposit. Stirring of the solution serves to prevent local depletion of the desired constituent at the electrode. It also brings about a better adhering deposit and allows a higher current density than otherwise would be possible.

The principle of the setup for electroanalysis is pictured in Fig. 40. The vessel containing the solution is a tall, lipless beaker of about 100

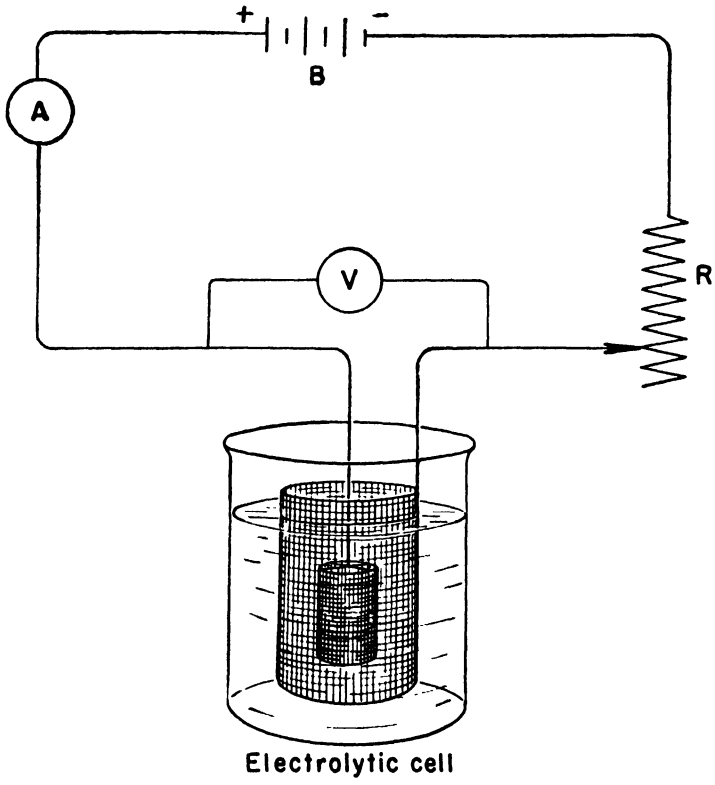


FIG. 40. Apparatus for electroanalysis. (*A*) Ammeter. (*B*) Source of direct current. (*R*) Resistance. (*V*) Voltmeter.

ml. size. The cathode is cylindrical platinum gauze of around 50 mesh per inch; it is about 2 or 3 cm. in diameter and 3 cm. in height. The anode may be a platinum spiral, or better, a cylindrical foil or gauze. It is preferably located within the cathode in a manner which allows it to be rotated so as to give a stirring effect.

The electrical current may be obtained from a storage battery, *B*, or from a 110-volt direct-current if such is available. (In the latter case a lamp bank resistance is inserted in the circuit in series with a rheostat which in turn is connected in parallel with the electrolytic cell. This will safely reduce the voltage.) The potential across the electrodes is recorded on the voltmeter, *V*, and the amperage is registered on ammeter, *A*. *R* is a variable resistance. To prevent loss of solution the beaker should be covered with a split watch glass.

ELECTROLYTIC DETERMINATION OF COPPER

The analysis of copper is carried out with a solution of copper sulfate acidified with sulfuric and nitric acids. At the cathode the reactions,

$$Cu^{++} + 2e \rightarrow Cu$$

and

$$2H^+ + 2e \rightarrow H_2$$

take place, and at the anode,

$$2OH^- - 2e \rightarrow \tfrac{1}{2}O_2 + H_2O$$

If hydrogen is liberated too vigorously at the cathode the deposited copper will be less compact. The acidity of the solution therefore must be carefully regulated. Nitric acid helps in the electrolysis of copper solutions since it acts as a depolarizer of hydrogen and prevents its excessive discharge. It oxidizes hydrogen ion at the cathode thus:

$$NO_3^- + 10H^+ + 8e \rightarrow NH_4^+ + 3H_2O$$

Obviously this reaction increases the pH of the solution and if the electrolysis is continued over a long period of time it may be necessary to add more acid.

Nitrate ion also may be reduced in part to nitrite ion,

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O$$

and the resulting nitrous acid tends to hold back the deposition of copper and also to oxidize the copper which is deposited to copper oxide. It is advisable, therefore, to boil the nitric acid which is to be used in order to free it of oxides of nitrogen; furthermore, a small amount of urea may be added to the electrolyzed solution since it will destroy any nitrous acid:

$$2HNO_2 + (NH_2)_2CO \rightarrow 2N_2 + CO_2 + 3H_2O$$

Any metal with a decomposition voltage much below 2 volts must be absent from the solution, and the presence of iron is objectionable for two reasons: in the ferric state it interferes with the deposition of copper, and, in addition, when reduced by the current to the ferrous state it may convert the nitrate ions to nitrite ions. Small amounts of iron, however, are not objectionable. If the deposit of copper is darker than a salmon color, either other metals have been deposited or some oxidation of copper to copper oxide has taken place.

Procedure. Prepare a solution of around 100 ml. containing an accurately weighed sample of about 0.2 to 0.4 g. The sample should be in the form of turnings or of shot, and should be washed with benzene to remove any oil. Add 2 ml. of concentrated sulfuric acid and 1 ml. of freshly boiled, concentrated nitric acid. Clean the electrodes in dilute nitric acid, rinse first with water and then with alcohol. Dry the cathode in the oven at 105° for 10 minutes, cool in the desiccator and weigh.

Remember not to touch the cathode with the fingers as this not only leads to errors in weighing but also may impart grease to the gauze cathode and thereby prevent a firm deposit of copper. Connect the cathode to the negative terminal of the apparatus and the anode to the positive terminal. Be sure that the stirring mechanism rotates freely.[3] Raise the beaker containing the copper solution into position. The electrodes should extend almost to the bottom of the beaker. The solution now should almost but not completely cover the electrodes; distilled water may be added if necessary. Cover the beaker with a split watch glass and turn on the stirring motor at a speed which does not cause spattering. Cut in the maximum resistance so that only a minimum current will flow and then close the electrolytic circuit. Adjust the voltage to 2 to 4 volts and the amperage to about 2 amperes. After 30 to 45 minutes the blue color should have disappeared. Then rinse off the watch glass into the beaker until the level of the solution is just above the top of the cathode. Replace the split watch glass, reduce the amperage to not over 1 ampere and continue the electrolysis for 10 minutes. If the newly immersed portion of the cathode shows no deposit the electrolysis may be considered complete. In case a new deposit of copper is formed during the last 10 minutes add a few milliliters of water and electrolyze 10 or 15 minutes longer. Then observe whether or not the stem of the cathode shows any evidence of copper. If so add 0.2 g. of urea and electrolyze another 15 minutes. When the process is judged complete, stop the stirring motor and remove a half milliliter of solution with a pipet. Test this for copper by adding ammonium hydroxide in excess. If a blue color develops return the test portion to the beaker and continue electrolyzing until the copper is completely deposited.

When the electrolysis is complete, turn off the stirring motor and lower the beaker, without cutting off the current, while continuously playing a stream of water from the wash bottle against the withdrawing cathode. As long as sufficient voltage is applied the solvent effect of the nitric acid on the deposited copper is negligible; thus the current is not turned off until the cathode has been completely removed from the solution. Finally rinse off the cathode by dipping several times into distilled water and then in successive portions of alcohol. Place the clean cathode in the drying oven at 105° for 2 or 3 minutes. Cool it in the desiccator and weigh. From the increased weight of the cathode calculate the percentage of copper in the sample. The duplicate determination should check within 0.2 per cent. Remove the copper on the cathode by dipping in concentrated nitric acid.

[3] The electrolysis may be carried out without stirring. In this case adjust the resistance so that a current of 0.5 ampere flows and continue the electrolysis overnight under a potential of about 2 volts.

DETERMINATION OF COPPER AND NICKEL (AND IRON)

Copper and nickel may be determined electrolytically in alloys such as monel metal and copper-nickel coinage alloys which contain only a small quantity of iron. The copper is deposited from the acid solution of such alloys, leaving the nickel and iron in solution. Before the nickel is electrodeposited any nitric acid which may be present is removed by evaporation in the presence of sulfuric acid and the iron is eliminated by double precipitation with ammonium hydroxide. The nickel remains as the nickel ammonia complex, $Ni(NH_3)_4^{++}$, which imparts the characteristic blue color to the solution.

Procedure. Accurately weigh a clean sample of the alloy of about 0.3 to 0.5 g. and transfer to a 150 ml. beaker. Dissolve the sample by adding 10 ml. of water, 1 ml. of concentrated sulfuric acid and 2 ml. of concentrated nitric acid. When solution is complete boil gently to expel oxides of nitrogen and then dilute to 100 ml. and deposit the copper electrolytically as described in the preceding section.

Evaporate the solution from the copper deposition on a hot plate until sulfuric acid fumes appear. This will expel all excess nitric acid. Cool the solution and add cautiously 25 or 30 ml. of water. Precipitate the ferric iron by adding to the warm solution about 10 ml. of 1:1 ammonium hydroxide in excess. This converts the nickel to the blue $Ni(NH_3)_4^{++}$ complex and the iron into hydrated ferric oxide. Transfer the precipitate to a small filter paper and collect the filtrate and washings in a tall-form beaker. After washing the precipitate three or four times with hot water, place the original beaker under the funnel, dissolve the precipitate by treating with 5 ml. of 1:6 sulfuric acid and wash the paper. Reprecipitate the iron with ammonium hydroxide, filter through the same filter paper and wash, receiving the filtrate and washings in the beaker containing the first filtrate. If the percentage of iron is to be determined the precipitate is ignited to ferric oxide and weighed; otherwise discard the precipitate. To the ammoniacal solution of nickel add 15 ml. of concentrated ammonium hydroxide and dilute to 100 to 125 ml. Electrolyze this solution for nickel using either the fast method (with stirring) or the slow (overnight) method and with the same current strength and potential as specified for the copper electrolysis. Wash the cathode with water and with alcohol, dry and weigh. From the weight of the deposited nickel calculate the percentage. Duplicate determinations should check within 0.2 per cent. Remove the nickel from the cathode by dissolving it in concentrated nitric acid. The nickel deposit can hardly be distinguished from the platinum of the electrode and its complete removal can be assured only by immersing the cathode in the hot nitric acid for from 15 to 30 minutes.

ANALYSIS OF BRASS

There are brasses of many different compositions,[4] but all contain copper and zinc as the chief or the only components; in addition some contain small amounts of lead, tin and iron. The determination of these metals in a given sample of brass affords an excellent example of determining the several components by different methods, since tin, iron and zinc are usually determined by chemical precipitation of one of their compounds while the other two metals are isolated electrolytically.

Tin is separated from the solution of the brass as hydrous stannic oxide; iron is precipitated as hydrous ferric oxide and zinc as zinc ammonium phosphate; copper and lead are electrolytically deposited, the former at the cathode and the latter as lead dioxide at the anode.

Procedure for Tin. Weigh accurately a sample of about 1 g. of clean brass and place in a 150 ml. beaker. Add 15 ml. of concentrated nitric acid. The action may start slowly, but do not heat rapidly at first or the fuming spray may result in loss of some of the sample. After solution is complete evaporate over a hot plate to about 5 or 10 ml. Cool, moisten with 5 ml. of concentrated nitric acid and warm over the hot plate for 5 minutes. Next, dilute to about 50 ml. with water and digest just below the boiling point for 15 minutes. If the precipitated hydrous oxide, which we may write as metastannic acid ($3Sn + 4HNO_3 + H_2O = 3H_2SnO_3 + 4NO$), comes out in large quantity, add a small amount of macerated filter paper pulp. This will facilitate the filtration of the precipitate. Filter while hot using a 9 cm. filter paper. Wash 10 times with hot 1:20 nitric acid. Collect the filtrate and washings and begin evaporating to a volume of 100 ml. for the determination of the other components. Partly dry the residue and filter paper, transfer to a porcelain crucible, char at low temperature and ignite over a Meker burner for 30 minutes or until white. Cool and moisten with a drop or two of nitric acid. Heat gently to drive off the excess acid and ignite to a constant weight. From the weight of SnO_2 calculate the percentage of tin in the sample. Duplicate results should not differ by more than 0.1 per cent.

Notes. The loss of metastannic acid as a colloidal suspension often causes low results. The use of macerated paper pulp (Schleicher and Schull Co.) reduces this source of error. Uncontaminated stannic oxide is practically pure white. If the ignited residue is brownish it is probable that some iron has been coprecipitated. A dark gray color indicates cupric oxide, the result of incomplete washing of the precipitate. Reduction of stannic oxide by carbon of the filter paper may occur during the ignition. A drop of nitric acid corrects this error. Metastannic acid loses its last trace of water very slowly, so a Meker burner, or a muffle furnace at 1100°, should be used for the ignition. If the percentage of tin must be known with the highest accuracy, the coprecipitation of other metals must be avoided. For

[4] See any handbook of chemistry and physics.

alternative methods of higher accuracy see Lord and Demorest, *Metallurgical Analysis*, The McGraw-Hill Book Co., New York, 1924, and Caley and Burford, *Ind. Eng. Chem., Anal. Ed.*, **8**, 114 (1936).

Procedure for Lead.[5] The filtrate from the tin determination should be evaporated to a volume of about 100 ml. Then place the solution in a 150 ml. lipless beaker and add 10 ml. of concentrated nitric acid and 2 or 3 drops of concentrated sulfuric acid. When this solution is electrolyzed between platinum electrodes, lead is deposited on the anode as PbO_2:

$$Pb^{++} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e$$

Weigh a clean, preferably sand-blasted, platinum gauze electrode. Connect it to the positive terminal, and a platinum spiral or foil electrode to the negative terminal. Then place the beaker containing the solution around the electrodes so that the latter are nearly, but not completely, submerged. Adjust the current to an amperage of about 1.5 amperes and the voltage to around 2 to 2.5 volts. Electrolyze the solution for an hour or more; then add a small amount of water and continue the electrolysis for 15 minutes. If no further deposit appears on the newly immersed portion of the anode the deposition is complete; the beaker is then lowered from around the electrodes while water is played from the wash bottle over the anode. Turn off the current when the electrodes are free from the solution. Disconnect the anode, dip in a beaker of water several times, then in alcohol or acetone, and dry it for 1 hour at 120°. The increase in weight of the anode represents the lead dioxide. Since the composition of the deposit is not exactly that corresponding to PbO_2, use the value 0.864 for the Pb/PbO_2 factor instead of the theoretical value of 0.866 in calculating the weight of lead in the deposit. Clean the electrode by dipping into a mixture of dilute nitric acid and hydrogen peroxide, and then rinsing in water. For alloys containing about 0.25 per cent of lead, duplicate results should agree within 0.02 per cent.

Notes. The solution must be rather strongly acidified with nitric acid, since otherwise some of the lead may be deposited on the *cathode*.

Interfering elements include antimony, bismuth, manganese, silver and tin. If these are present the PbO_2 is contaminated with their oxides. No anion except sulfate and nitrate should be present.

A small quantity of sulfuric acid is added to promote a more adherent deposit of PbO_2.

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[5] Copper and lead may be deposited simultaneously from a solution containing both ions, the former as such on the cathode and the latter as the dioxide on the anode. For directions for the simultaneous method see, for example, Scott, *Standard Methods of Chemical Analysis*, 5th ed., D. Van Nostrand Co., New York, 1939, p. 1355.

Lead also may be determined gravimetrically by precipitating as $PbSO_4$ (see p. 274).

The factor 0.864 instead of the theoretical 0.866 is used because a small but practically constant proportion of the total weight of the deposit is due to water retained, even after drying at 120° for an hour, by the PbO_2.

If the solution electrolyzed contains more than 0.1 g. of lead, a smaller portion of the solution should be used for the electrolysis. Larger amounts of lead usually cause a sloughing off of some of the deposited PbO_2.

In cleaning the electrode of the PbO_2, nitric acid alone will not suffice since PbO_2 is insoluble in nitric acid. Hydrogen peroxide acts as a reductant toward PbO_2,

$$PbO_2 + H_2O_2 + 2H^+ \rightarrow Pb^{++} + O_2 + 2H_2O$$

and thus aids in cleaning the electrode.

Procedure for Copper. The solution from which the lead has been deposited contains the copper, iron and zinc and is next electrolyzed for copper. Add ammonium hydroxide slowly, stirring with the previously used cathode which is still in the beaker, until the first permanent precipitate of copper hydroxide or the blue $Cu(NH_3)_4^{++}$ color appears. Then add freshly boiled concentrated nitric acid until just acidic, then 1 or 2 ml. in excess, and 2 ml. of concentrated sulfuric acid. Proceed with the electrolysis as already described under Determination of Copper, p. 309. After the copper has been deposited save the solution for the determination of iron and zinc.

Procedure for Iron. Add 1 ml. of bromine water to the solution from the electrolysis of lead and copper, and simmer gently for 5 minutes or until the excess bromine is expelled. Add concentrated ammonium hydroxide until a permanent precipitate is obtained and then 10 ml. excess. Filter the precipitated hydrous iron oxide on a small quantitative filter paper and wash three times with 1:100 ammonium hydroxide. Redissolve the precipitate by pouring 20 ml. of 1:2 hot hydrochloric acid through the filter, and catch the solution in the precipitation beaker. Wash the paper with water five times. Now reprecipitate the iron with concentrated ammonium hydroxide, adding 5 ml. excess. Filter in the same paper as was used the first time. Wash with 1:100 ammonium hydroxide five or six times. Combine the two filtrates and reserve for the zinc determination. Ignite the precipitate to Fe_2O_3, weigh and calculate the percentage of iron in the sample. The deviation should not exceed a few hundredths per cent for duplicate determinations.

Notes. During the electrolysis ferric iron was largely reduced at the cathode to ferrous iron. Bromine reoxidizes ferrous iron to ferric iron.

Zinc is not precipitated when an excess of ammonia is used, since it forms the complex $Zn(NH_3)_4^{++}$ ion. Double precipitation of the hydrous iron oxide is necessary in order to minimize the coprecipitation of zinc.

Procedure for Zinc. To the combined filtrates from the iron determination add 25 ml. each of hydrochloric and nitric acids and evaporate

nearly to dryness or until sulfuric acid fumes are evolved. Add 2 ml. of hydrochloric acid, dilute to 50 ml. and filter off the silica present, if any. Wash thoroughly and dilute the filtrate to 150 ml. (If no silica was present dilute to 150 ml. immediately after adding the 2 ml. of hydrochloric acid.) Add several drops of bromthymol blue, then add concentrated ammonium hydroxide until the solution is greenish. Heat to a temperature just below boiling and add slowly 25 ml. of freshly prepared 2 *M* solution of diammonium hydrogen phosphate. Digest over a steam bath for half an hour and allow to cool for 1 hour or longer before filtering. Filter through a Gooch crucible. Wash the precipitate with 0.1 *M* solution of diammonium hydrogen phosphate until washings are free from chlorides and then three times with 50 per cent alcohol. Dry for 1 hour at 105°, after which ignite with a Meker burner or in a muffle furnace at 900° for 20-minute periods until a constant weight is obtained. From the weight of $Zn_2P_2O_7$ calculate the percentage of zinc in the sample. Duplicate determinations should show a relative mean deviation of 2 parts per 1000 or less.

Notes. The addition of a considerable quantity of concentrated hydrochloric and nitric acids is necessary to destroy the ammonium salts which accumulated during the preceding analyses. The solution of diammonium hydrogen phosphate should not contain any of the monoammonium salt. Test a small portion of the solution with phenolphthalein. If not slightly pink add ammonium hydroxide until the faintest pink color is noticed.

The precipitate is washed first with the diammonium hydrogen phosphate solution since the salt tends to hydrolyze in warm water. The washing with 50 per cent alcohol removes the phosphate solution from the precipitate and promotes drying.

Questions and Problems

1. What would be the effect on the electrode potential if sodium chloride were added to a solution of silver nitrate in which a silver electrode is immersed?
2. The equilibrium concentration of zinc (the concentration of Zn^{++} ions at which there would be zero potential between the metal and its ions) is approximately 10^{41}. Obviously no zinc salt is sufficiently soluble to establish such a high concentration. How, nevertheless, may this value be experimentally confirmed?
3. One faraday of electricity will deposit how many grams of the following: copper, silver, cobalt, lead as PbO_2?
4. If an acid solution is electrolyzed between platinum electrodes overnight (say 10 hours) at a current of 1 ampere, what volume of hydrogen (at 0° and 760 mm.) will be liberated at the cathode?
   Answer: 4.18 l.
5. What amperage is necessary in order to deposit 5.0 g. of zinc from a solution of zinc sulfate in exactly 1 hour?
   Answer: 4.1.

6. (a) Calculate the theoretical decomposition voltage for a 1 *M* solution of zinc iodide. (b) What will be the theoretical decomposition voltage after the concentration of Zn^{++} ion has decreased to 0.001 molar?
   Answer: (a) 1.28 volts; (b) 1.56 volts.
7. Given a solution containing copper sulfate and 0.5 *M* nickel sulfate. Assuming a constant voltage between the decomposition voltages of the two salts, and ignoring overvoltage effects, calculate the concentration of Cu^{++} ion which will prevail when the nickel first begins to deposit.
   Answer: 5.4×10^{-21}.
8. Make a calculation similar to that of (7) for the concentration of Ni^{++} ion prevailing when cobalt begins to deposit from a solution containing nickel sulfate and 1 *M* cobalt sulfate.
   Answer: 9.1×10^{-3}.
9. Confirm the statement on p. 306 that if the hydrogen overvoltage is 0.6 volt (remember that this makes the effective value for $E^0_H = -0.6$), zinc ions will continue to deposit even when the concentration is 10^{-5}, provided the pH is 5.2.
10. Prove that with no hydrogen overvoltage zinc cannot be deposited from a neutral solution (i.e., compute the concentration of Zn^{++} ion necessary for the simultaneous liberation of zinc and hydrogen).

Chapter 19

COLORIMETRY[1]

Analysis by colorimetric methods depends upon the absorption of light which passes through colored solutions of the constituent being determined. Very small amounts of a constituent may be determined in this way; in fact too deeply colored solutions as a rule are unsuited for colorimetric analysis. The method is usually more rapid than volumetric and gravimetric analyses. In particular colorimetry furnishes a convenient means of determining the composition in regard to a constituent, the presence of a small quantity of which produces a marked effect upon the material of which it is a part: for example, small amounts of certain components in steel, traces of impurities in chemical reagents and the like. The error involved in colorimetric analyses usually runs to at least 10 to 20 parts per 1000. Nevertheless, with further refinements in equipment and methods, it seems that greater accuracy is likely to be attained. Willard and Ayres[2] point out that it is possible frequently to apply colorimetric analysis to concentrated solutions with results comparable in accuracy with gravimetric or volumetric methods. They secured best results in the determination of iron, using their thermoelectric absorptiometer, when the concentration of iron was from 15 to 40 g. per liter.

The laws upon which this method of analysis are based were stated years ago.[3] Lambert showed that the amount of monochromatic light which is absorbed by a liquid through which it passes is proportional to the intensity of the incident light, and that the intensity of the light which is transmitted varies inversely with the length of the path it traverses through the liquid. Beer found that the intensity of the transmitted light is inversely proportional to the concentration of the colored solution. If we let I_0 represent the intensity of the incident light, I_t the intensity of the transmitted light traversing a layer of colored liquid of thickness t, and C the concentration of this solution, the above laws may be expressed mathematically as

$$\ln \frac{I_t}{I_0} = -kCt$$

[1] See Yoe, *Photometric Chemical Analysis*, John Wiley & Sons, New York, 1928, for an extensive treatise.

[2] Willard and Ayres, *Ind. Eng. Chem., Anal. Ed.*, **12**, 287 (1940).

[3] Lambert, *Photometria sive de mensura et gradibus luminis, colorum et umbrae* (1760); Beer, *Ann. Physik*, (2) **86**, 78 (1852).

where k is a proportionality factor specific for each particular colored solute. Changing from the natural to Briggsian logarithm only changes the constant by the factor 0.4343 so that we have

$$\log \frac{I_t}{I_0} = -KCt$$

Taking the antilogarithm of both sides we have

$$\frac{I_t}{I_0} = 10^{-KCt}$$

or

$$I_t = 10^{-KCt} I_0$$

Suppose that we prepare two solutions colored by the same solute, one of a known concentration, the other unknown. A beam of light is split and passed through the two solutions. If the light transmitted through the solutions is of equal intensity then

$$I_t = 10^{-KCt} I_0 = 10^{-KC't'} I_0$$

from which it follows that

$$Ct = C't'$$

or

$$C:t' = C':t$$

It is obvious that in any analysis the actual values of K and I need not be known; the final equation above simply states that the concentrations of the two solutions are inversely proportional to the thickness of the two layers of the solutions transmitting the light. It is this principle upon which the colorimeter is based, and the instruments developed to analyze solutions by this method are designed to make easy the matter of varying t and t' until the intensity of the light passing through the solution of known concentration equals that of the light passing through the solution of unknown concentration. When this is the case we have, among the four factors of the last equation above, a known concentration and the measurable factors t and t'; therefore the concentration of the unknown solution is calculable.

In order to analyze a solution colorimetrically it is necessary (a) that the unknown constituent give a colored solution or else be capable of conversion into a soluble colored compound; (b) that only one colored substance be present; and (c) that the solution of known concentration not only contain the same constituent as the unknown solution, but also contain any other substances present in the unknown and in about the same quantities. From (c) it follows that the preparation of the standard

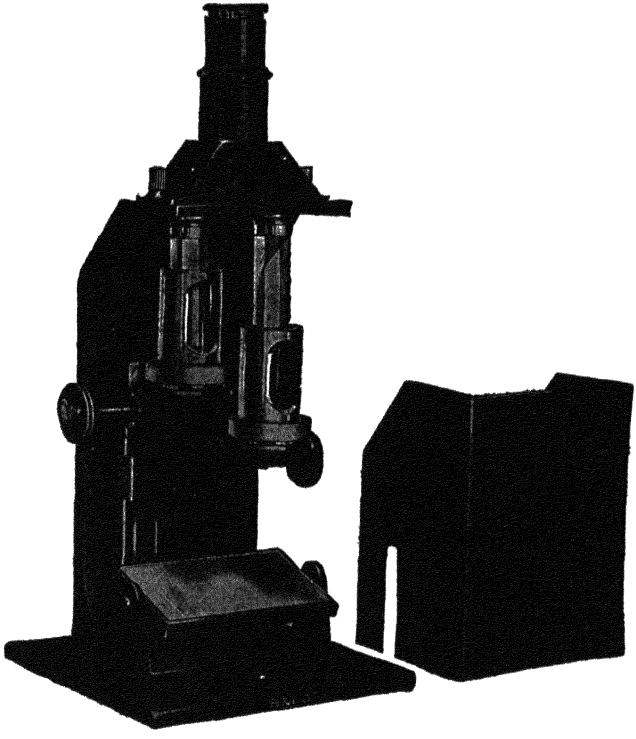

FIG. 41. A colorimeter. (Courtesy, Popoff: *Quantitative Analysis*, Philadelphia, The Blakiston Company.)

(known) solution should be carried out in the same manner as the unknown.

The Colorimeter. This instrument, Fig. 41, provides the means for passing light from a single source through the standard solution and the unknown solution, and for adjusting the lengths of the two paths along which the light penetrates the solutions so that equal, transmitted intensities are obtained. The two distances l and l' may be read from the instrument.

Briefly, the beam of light is split into two pencils which are reflected by a mirror to an observing microscope. One pencil of rays passes through a glass cup containing the standard solution and the other passes through a cup containing the unknown solution. A plunger fits into each of the cups and may be located at any height in the cup by raising or lowering the latter by means of a pinion. Both plungers and cups have optically plane glass bottoms. By varying the height of the plunger in its cup the thickness of the solution through which the light penetrates is varied, and the position of each plunger in the cup is read from a graduated scale. There is a compound prism between the ob-

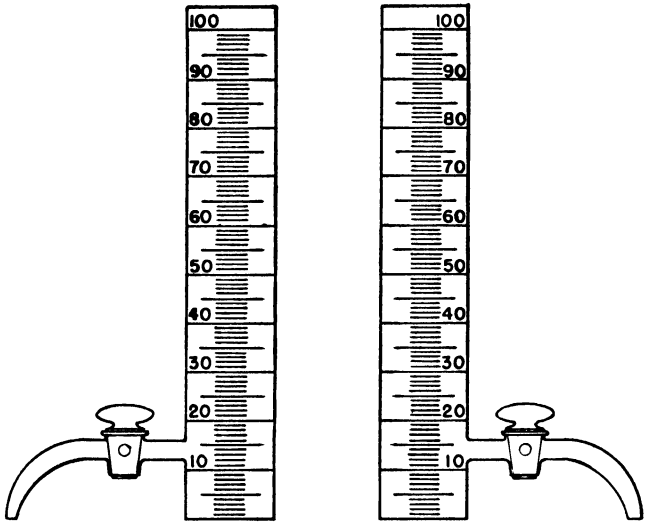

FIG. 42. Hehner cylinders.

serving microscope and the plungers which brings the two beams of light to a common axis so that the intensities of the two beams are observed in two adjacent fields, making the matching of intensities a simple matter.

The two halves of the field of illumination must be matched *before* an analysis is started. Then the standard solution is placed in one cup and the unknown in the other. Next the plunger is located about midway in the former cup, after which the position of the plunger in the cup containing the unknown is moved until the light in the two half-fields appears of identical intensity. Obviously the two solutions must be prepared of nearly the same concentration, else the plungers might be incapable of effecting a sufficient difference in the thickness of the solutions through which the beams of light pass to compensate for the difference in concentration. It then would be impossible to obtain equal intensities in the two half-fields. In such a circumstance the unknown solution may be diluted quantitatively, or a standard solution of different concentration may be substituted, so that the height of the two plungers will not differ greatly.

Recently greater precision in colorimetry has been secured by the development of the electrophotometer, which substitutes a photoelectric cell for the eye in determining color intensity. The chief advantage is greater sensitivity and the elimination of the personal element in judging light intensity. An article by Muller[4] describes the design and the characteristic features of many types of photoelectric equipment, and includes an extensive bibliography.

[4] Muller, *Ind. Eng. Chem., Anal. Ed.*, **11**, 1 (1939).

If a colorimeter is not available a simpler method of analysis involving the same principle may be employed, but with less accurate results, by using Hehner cylinders (Fig. 42). These are pairs of tall, graduated cylinders having uniform bores and plane, flat bottoms. They are equipped with stopcocks about 2.5 cm. from the bottom through which the solution, either standard or unknown (whichever is darker in color), may be withdrawn until the colors in the cylinders match one another when viewed from above. The reading of the menisci then may be taken and from the relationship, $Cl = C'l'$, the concentration of the unknown solution may be calculated.

An equally simple method of making color comparisons in the analysis of a colored unknown is by the use of Nessler tubes. A series of standard solutions containing definite and slightly differing amounts of the constituent are prepared. Equal volumes of these known solutions are placed in Nessler tubes. The tubes (Fig. 43), of course, are of equal bore and have plane glass bottoms. The range of concentrations of these standards must include the concentration of the constituent in the unknown solution. The latter is placed in another Nessler tube and matched against the standards by viewing from above. The standard solution showing the same intensity of color as the unknown solution represents the concentration of the latter. A satisfactory degree of accuracy is attained by making the difference in concentration of the successive standards in the series very small. The illumination should be entirely from the bottoms of the tubes.

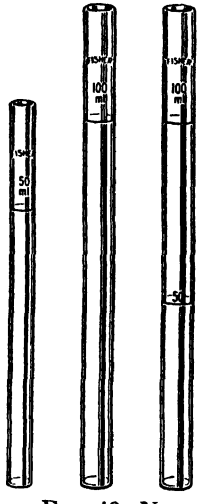

FIG. 43. Nessler tubes. (Courtesy, Fisher Scientific Co.)

The hydrogen ion concentration of a solution is often measured colorimetrically. The reader should consult the standard reference works for details regarding the various methods employed. One method is based upon the different hues of color exhibited by indicators when added to solutions of definite hydrogen ion concentration. A series of buffer solutions (see p. 97) each of known hydrogen ion concentration is prepared. The whole series varies by a constant amount from one solution to the next, say by 0.2 pH unit. A certain number of drops of a given indicator is added to 10 ml. of those standard (buffer) solutions coming within its range (see p. 100). A different tint of color results in these several solutions. Other indicators are used similarly for different pH spans covered by other members of the series of buffer solutions.

To 10 ml. of the unknown solution, in a tube identical with those containing the now variously colored standards, is added the same num-

ber of drops of appropriate indicator. The color developed is matched against the standards and thus the pH of the unknown, with a possible error of 0.1 pH unit, is revealed. Since each indicator covers only a limited pH range, some preliminary testing of the unknown is necessary in order to know which indicator to employ—i.e., which indicator will include within its range the pH value of the unknown.

A modification of the above technique is to use, instead of the colored buffer solutions, a series of colored glass standards. The pieces of glass, of course, must match the colors given by the indicators in the series of buffer solutions. The advantage of the glass standards is their durability. Their chief disadvantage is that their colors do not always reproduce perfectly those obtained with the indicators and the buffer solutions.

Determination of Manganese in Steel

The manganese in steel is oxidized to permanganate by treating a nitric acid solution of the sample with potassium periodate.

$$2Mn^{++} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

Since the sample contains iron, phosphoric acid is added to prevent the color of ferric ions by forming a colorless complex ion with the iron. The solution is then diluted to a definite volume and its color compared with a solution prepared in an identical manner from a steel of known manganese content. If a manganese steel of known composition is not available a permanganate solution of manganese content comparable with that of the unknown steel solution may be prepared by accurately diluting a standard permanganate solution.

Procedure. Accurately weigh a sample of 0.5 to 1 g. both of the unknown and of the known sample of steel. Treat each as follows. Dissolve in 50 ml. of 6 *N* nitric acid. After solution is complete, boil gently for 2 minutes to remove oxides of nitrogen. Add 1 g. of ammonium persulfate and boil 10 minutes to oxidize carbon compounds and destroy the excess persulfate. Dilute to about 100 ml. and add 25 ml. of 6 *M* phosphoric acid and 0.5 g. of potassium periodate. Boil for 5 minutes or, if no purple color appears, add further 0.5 g. portions of the periodate and continue boiling until a purple color does appear. Cool the solution, transfer to a 250 ml. volumetric flask and dilute to the mark.

The colorimeter is set up for use as follows: Place the instrument in a location which will give a good source of diffused daylight, preferably a northern exposure. (A white artificial source of light may be used if preferred.) Check the instrument for matching by placing portions of the standard solution in each cup, first giving both cups and plungers a triple rinse with the solution. The cups are filled only half full to avoid overflow when they are raised. Carefully raise the cups until the plungers are just

in contact with the bottoms of the cups. The scales should now give 0.0 mm. readings; if they do not, note the reading of each and apply this as a correction when the analysis is made. Arrange the position of the instrument and the mirror so that the two adjacent fields show equal intensities. Then lower the right cup until the plunger is about midway in the cup and at a whole-number scale reading. Adjust the liquid depth in the other cup until the two halves of the field are of the same color and intensity. Record the scale reading of the left cup. Change the position of the left cup and repeat the matching three times from random positions of deeper color and three times from positions of lighter color. Greater precision is obtained by the average of the several independent readings. (The average deviation from the mean should be 0.2 scale division or less, and the mean of the readings of the one cup should check the mean of the readings of the other cup within 10 parts per 1000.)

ANALYSIS. Empty the left cup and, after three rinsings with the unknown solution, half fill it with the unknown. With the right cup remaining at its original midway setting, proceed to match the color intensities six or more times exactly as was done in checking the instrument.

It is well to duplicate the analysis repeating the procedure with new portions of both known and unknown solutions, and, if necessary, to adjust the concentration of the unknown to a manganese content of 5 mg. or less per 250 ml. of solution.

From the average of the readings and the manganese content of the known solution, calculate the percentage of manganese in the sample. Use the equation, $Cl = C'l'$. The absolute error may amount to 0.01 per cent.

Notes. Any error due to a difference of light intensity of the two fields or to other instrumental defects may usually be revealed by interchanging the standard and the unknown solutions so that the unknown is in the right cup.

In repeating the analysis the concentrations of the solutions may be brought closer to one another if they are not approximately the same already; Beer's law shows almost no deviation if the concentrations are nearly equal.

Since the color of a solution may be seriously affected by the presence of foreign ions it is better that the standard solutions be made up from a steel of known manganese content, rather than from a standardized potassium permanganate solution, in order that the standard and the unknown solutions may be nearly alike in composition.

APPENDIX

Care of Platinum Ware 327
References 329
Tables 331
Ionization constants of some bases 331
Ionization constants of some acids 331
Solubility products 332
Formula weights 333
Specific gravity of ammonia solutions 335
Specific gravity of strong acids 336
Logarithms 338

CARE OF PLATINUM WARE

PLATINUM crucibles and dishes should be handled with care, for the metal is so soft that the vessels are easily dented. Small dents may be pressed out if a wooden form is available which closely fits into the vessel. Lacking this, gentle pressure from the rounded end of a test tube may be employed to restore the crucible or dish to its original shape.

After platinum ware has been used it should be cleaned immediately. This usually may be accomplished by placing in boiling 1:1 hydrochloric acid. If this fails to remove all stains the platinum should be immersed in fused potassium bisulfate for a few minutes, after which the salt crystals are removed by means of hot water. Fused sodium carbonate and borax also are used as cleaning fluxes. Stains which are not removed by the above cleansing sometimes yield to heat treatment in a muffle furnace at 1000° to 1100° for 10 hours. This may succeed in bringing base metals to the surface of the platinum, after which 1:1 hydrochloric acid will dissolve the contaminant.

When the platinum is clean it should be burnished by rubbing the vessel inside and outside, using fine, round grains of sea sand moistened with water. The rubbing may be done with the finger or a soft rubber eraser may be used. This will give a polish to the platinum and will remove the freckles which often may be seen on a newly cleaned vessel and which may be due to an incipient crystallization on the metal surface. If this is not destroyed by burnishing it may spread through the platinum and finally bring about cracking of the metal. After polishing with sand, the platinum should be rinsed with acid, then with water, dried and ignited.

In making ignitions by means of a burner, only the upper, nonluminous part of the flame should touch the platinum. The reducing zone of the flame contains unburned gas and this leads to the crystallization of the metal already mentioned.

Substances of unknown composition should never be heated in platinum ware. In particular the following points should be kept in mind:

1. Substances containing antimony, arsenic, bismuth, copper, tin, lead, mercury and silver may yield the free metal which, having low melting points, would alloy with the platinum.

2. Substances likely to give free chlorine or bromine would cause oxidation of the platinum. Therefore, fusions or evaporations in which these elements are set free must be carried out in dishes other than platinum.

3. Small amounts of free sulfur or phosphorus will make platinum very brittle. Thus fusions of phosphates or phosphides, sulfates or sulfides, if reducing agents are present, must be carried out with great care.

4. Platinum is attacked at high temperatures by the alkaline earths, caustic alkalies, nitrates, nitrites and cyanides. Fusions with these substances therefore must not be made in platinum vessels.

Hot platinum ware should be handled with platinum-tipped tongs and only triangles made of platinum, clay or quartz should be used to support platinum vessels during heating.

If in spite of all precautions a piece of platinum is indelibly stained, it may be returned to a manufacturer of platinum ware in exchange for a new piece, usually at a quite reasonable cost.

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TABLES

TABLE I. IONIZATION CONSTANTS OF SOME BASES (*Room Temperature*)

Base	K_b
Ammonium hydroxide	1.8×10^{-5}
Aniline	4.6×10^{-10}
Caffeine	4.1×10^{-14}
Ethylamine	5.6×10^{-4}
Hydrazine	3×10^{-6}
Methylamine	4.4×10^{-4}
Pyridine	2×10^{-9}

TABLE II. IONIZATION CONSTANTS OF SOME ACIDS

(*Room Temperature*)

Acid	K_a	*Acid*	K_a
Acetic	1.8×10^{-5}	Oxalic	
Benzoic	6.6×10^{-5}	K_{a_1}	3.8×10^{-2}
Boric	6.0×10^{-10}	K_{a_2}	1.9×10^{-5}
Carbonic		Phosphoric	
K_{a_1}	3.0×10^{-7}	K_{a_1}	8.0×10^{-3}
K_{a_2}	6.0×10^{-11}	K_{a_2}	7.5×10^{-8}
Citric		K_{a_3}	5.0×10^{-13}
K_{a_1}	8.7×10^{-4}	Phthalic	
K_{a_2}	1.8×10^{-5}	K_{a_1}	1.3×10^{-3}
K_{a_3}	4.0×10^{-6}	K_{a_2}	3.1×10^{-6}
Formic	1.8×10^{-4}	Salicylic	1.1×10^{-3}
Hydrocyanic	2×10^{-9}	Sulfurous	
Hydrofluoric	1.7×10^{-5}	K_{a_1}	1.7×10^{-2}
Hydrogen sulfide		K_{a_2}	6.2×10^{-8}
K_{a_1}	9×10^{-8}	Tartaric	
K_{a_2}	1.2×10^{-15}	K_{a_1}	1.1×10^{-3}
Nitrous	4.0×10^{-4}	K_{a_2}	6.9×10^{-5}

TABLE III. SOLUBILITY PRODUCTS

(Room Temperature)

Compound	$K_{s.p.}$	*Compound*	$K_{s.p.}$
$Ag[Ag(CN)_2]$	2.2×10^{-12}	FeC_2O_4	2.1×10^{-7}
$AgBr$	7.7×10^{-13}	$Fe(OH)_2$	2×10^{-14}
$AgBrO_3$	6.6×10^{-5}	FeS	3.7×10^{-19}
$AgCl$	1.1×10^{-10}		
$AgCNS$	1×10^{-12}	$Fe(OH)_3$	1.1×10^{-36}
Ag_2CO_3	6.2×10^{-12}		
Ag_2CrO_4	2.4×10^{-12}	Hg_2Br_2	3×10^{-23}
$Ag_2Cr_2O_7$	2.0×10^{-7}	Hg_2Cl_2	2×10^{-18}
AgI	1.5×10^{-16}	Hg_2I_2	4×10^{-29}
$AgIO_3$	1×10^{-8}	Hg_2S	1×10^{-47}
Ag_2S	2×10^{-49}		
		HgS	4×10^{-54}
$Al(OH)_3$	3.7×10^{-15}		
		$MgCO_3$	1×10^{-5}
$BaCO_3$	8.1×10^{-9}	MgC_2O_4	8.6×10^{-5}
BaC_2O_4	1.5×10^{-7}	MgF_2	7×10^{-9}
$BaCrO_4$	2.4×10^{-10}	$MgNH_4PO_4$	2.5×10^{-13}
BaF_2	1.7×10^{-6}	$Mg(OH)_2$	1.2×10^{-11}
$Ba(IO_3)_2$	6.5×10^{-10}		
$BaSO_4$	1.1×10^{-10}	$Mn(OH)_2$	4.5×10^{-14}
		MnS	1.4×10^{-15}
$CaCO_3$	8.7×10^{-9}		
CaC_2O_4	2.6×10^{-9}	$PbCO_3$	3.3×10^{-14}
$CaC_4H_4O_6$	7.7×10^{-7}	PbC_2O_4	2.8×10^{-11}
CaF_2	3.5×10^{-11}	$PbCrO_4$	1.8×10^{-14}
$Ca(IO_3)_2$	6.5×10^{-7}	PbF_2	3.7×10^{-8}
$CaSO_4$	6.1×10^{-5}	PbI_2	1.4×10^{-8}
		$Pb(IO_3)_2$	1.9×10^{-13}
CdC_2O_4	1.5×10^{-8}	$Pb(OH)_2$	2.5×10^{-16}
CdS	3.6×10^{-29}	PbS	3.4×10^{-28}
		$PbSO_4$	1.1×10^{-8}
CoS	1×10^{-27}		
		$SrCO_3$	1.6×10^{-9}
Cu_2Br_2	4.2×10^{-8}	SrC_2O_4	5.8×10^{-8}
Cu_2Cl_2	1.0×10^{-6}	SrF_2	2.8×10^{-9}
Cu_2I_2	5×10^{-12}	$SrSO_4$	3.8×10^{-7}
Cu_2S	2×10^{-47}		
		ZnC_2O_4	1.4×10^{-9}
CuC_2O_4	2.9×10^{-8}	$Zn(OH)_2$	1.8×10^{-14}
$Cu(IO_3)_2$	1.4×10^{-7}	ZnS	1.2×10^{-23}
CuS	8.5×10^{-45}		

TABLE IV. FREQUENTLY USED FORMULA WEIGHTS

Formula	Weight	Formula	Weight
$AgBr$	187.80	$HC_2H_3O_2$	60.05
$AgBrO_3$	235.80	HCl	36.47
$AgCl$	143.34	$HClO_4$	100.46
AgI	234.80	HSO_3NH_2	97.09
$AgNO_3$	169.89	$H_2C_2O_4$	90 04
Al_2O_3	101.94	$H_2C_2O_4.2H_2O$	126.07
$Al(OH)_3$	77.99	HNO_3	63.02
As_2O_3	197.82	HNO_2	47.02
As_2O_5	229.82	H_2O_2	34.02
As_2S_3	246.00	H_3PO_4	98 00
$BaCl_2$	208.27	H_2S	34.08
$BaCl_2.2H_2O$	244 31	H_2SO_4	98.08
$BaCO_3$	197.37	Hg_2Br_2	561.06
BaC_2O_4	225.38	Hg_2Cl_2	472.14
BaO	153.36	Hg_2I_2	655 06
$Ba(OH)_2$	171.38	KBr	119 01
$BaSO_4$	233.42	$KBrO_3$	167.01
$CaCl_2$	110.99	KCl	74.56
$CaCO_3$	100 09	$KClO_3$	122 55
CaO	56.08	$KClO_4$	138.55
$Ca(OH)_2$	74.10	KCN	65.11
$Ca_3(PO_4)_2$	310.20	K_2CO_3	138.20
$CaSO_4$	136.14	K_2CrO_4	194.20
$Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$	632.56	$K_2Cr_2O_7$	294.21
CH_3COOH	60.05	$KHC_4H_4O_6$	188.18
C_6H_5COOH	122.12	$KHC_8H_4O_4$	204.16
CO_2	44.01	KHC_2O_4	128 12
Cr_2O_3	152.02	$KHC_2O_4.H_2O$	146.14
CuO	79.54	$KHC_2O_4.H_2C_2O_4.2H_2O$	254 19
CuS	95.60	$KH(IO_3)_2$	389.94
Cu_2S	159 14	KI	166.02
$CuSO_4$	195 60	KIO_3	214.02
$CuSO_4.5H_2O$	249.68	$KMnO_4$	158.03
$FeCl_3$	162.22	KOH	56.10
$FeCl_3.6H_2O$	270.32	$MgCO_3$	84.33
$FeCO_3$	115.86	$MgNH_4PO_4$	137.33
FeO	71.85	MgO	40.32
Fe_2O_3	159.70	$Mg(OH)_2$	58.34
Fe_3O_4	231.55	$Mg_2P_2O_7$	222.60
$Fe(OH)_2$	89.87	MnO	70.93
$Fe(OH)_3$	106.87	MnO_2	86.93
$FeSO_4$	151.91	$Na_2B_4O_7$	201.27
$FeSO_4.7H_2O$	278.02	$NaBr$	102.91
$Fe_2(SO_4)_3$	399.88	$NaBrO_3$	150.91
$FeSO_4.(NH_4)_2SO_4.6H_2O$	392.15	$NaCl$	58.45
HBr	80.92	$NaCN$	49 02
$HCOOH$	46.03	Na_2CO_3	106 00

TABLE IV. FREQUENTLY USED FORMULA WEIGHTS—*Continued*

Formula	*Weight*	*Formula*	*Weight*
$Na_2C_2O_4$	134.01	PbO	223.21
$NaHCO_3$	84.01	PbO_2	239.21
NaI	149.92	Pb_2O_3	462.42
Na_2O	61.99	Pb_3O_4	685.63
NaOH	40.01	$PbSO_4$	303.27
Na_2S	78.05	P_2O_5	141.96
$Na_2S_2O_3$	158.11	Sb_2O_3	291.52
$Na_2S_2O_3.5H_2O$	248.19	Sb_2O_5	323.52
NH_3	17.03	Sb_2S_3	339.70
NH_4Cl	53.50	SiF_4	104.06
NH_4OH	35.05	SiO_2	60.06
N_2O	44.02	$SnCl_2$	189.61
NO	30.01	$SnCl_4$	260.53
N_2O_3	76.02	SnO_2	150.70
NO_2	46.01	ZnO	81.38
N_2O_5	108.02	$Zn_2P_2O_7$	304.72
$PbCrO_4$	323.22		

TABLE V. SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 15° C.*

(According to Lunge and Wiernik)

Specific gravity	*Per cent NH_3*	*Specific gravity*	*Per cent NH_3*
1 000	0.00	0 910.	15 63
0.998	0.45	0 938..	16 22
0.996	0.91	0 936.	16.82
0 994	1.37	0 934	17.42
0.992..	1.84	0 932.	18.03
0.990	2.31	0.930.	18.64
0.988	2.80	0.928.	19.25
0 986....	3.30	0.926....	19.87
0.984....	3.80	0 924..	20.49
0.982	4 30	0 922....	21 12
0 980	4 80	0.920.	21.75
0 978.	5.30	0 918...	22.39
0.976.....	5.80	0 916...	23.03
0.974	6.30	0 914.	23.68
0.972.	6.80	0 912..	24 33
0.970	7.31	0 910.	24.99
0 968...	7.82	0 908	25 65
0.966	8.33	0 906	26 31
0.964	8.84	0.904	26.98
0.962.....	9.35	0 902.	27 65
0.960	9.91	0 900	28.33
0.958..	10.47	0 898.	29.01
0.956...	11.03	0 896	29.69
0.954	11 60	0 894	30.37
0.952	12.17	0 892	31.05
0.950.	12.74	0 890	31.75
0.948....	13.31	0 888.	32.50
0.946...	13.88	0 886..	33.25
0.944.	14.46	0 884.	34.10
0.942.	15.04	0.882	34.95

* From Treadwell and Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons, Inc., by permission.

TABLE VI. SPECIFIC GRAVITY OF STRONG ACIDS AT $\frac{15°}{4°}$ IN VACUO*

(According to G. Lunge)

Specific gravity at $\frac{15°}{4°}$ *(vacuo)*	*Per cent by weight*			*Specific gravity at* $\frac{15°}{4°}$ *(vacuo)*	*Per cent by weight*	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.53	31.70
1.005	1.15	1.00	0.95	1.240	38.29	32.28
1.010	2.14	1.90	1.57	1.245	39.05	32.86
1.015	3.12	2.80	2.30	1.250	39.82	33.43
1.020	4.13	3.70	3.03	1.255	40.58	34.00
1.025	5.15	4.60	3.76	1.260	41.34	34.57
1.030	6.15	5.50	4.49	1.265	42.10	35.14
1.035	7.15	6.38	5.23	1.270	42.87	35.71
1.040	8.16	7.26	5.96	1.275	43.64	36.29
1.045	9.16	8.13	6.67	1.280	44.41	36.87
1.050	10.17	8.99	7.37	1.285	45.18	37.45
1.055	11.18	9.84	8.07	1.290	45.95	38.03
1.060	12.19	10.68	8.77	1.295	46.72	38.61
1.065	13.19	11.51	9.47	1.300	47.49	39.19
1.070	14.17	12.33	10.19	1.305	48.26	39.77
1.075	15.16	13.15	10.90	1.310	49.07	40.35
1.080	16.15	13.95	11.60	1.315	49.89	40.93
1.085	17.13	14.74	12.30	1.320	50.71	41.50
1.090	18.11	15.53	12.99	1.325	51.53	42.08
1.095	19.06	16.32	13.67	1.330	52.37	42.66
1.100	20.01	17.11	14.35	1.335	53.22	43.20
1.105	20.97	17.89	15.03	1.340	54.07	43.74
1.110	21.92	18.67	15.71	1.345	54.93	44.28
1.115	22.86	19.45	16.36	1.350	55.79	44.82
1.120	23.82	20.23	17.01	1.355	56.66	45.35
1.125	24.78	21.00	17.66	1.360	57.57	45.88
1.130	25.75	21.77	18.31	1.365	58.48	46.41
1.135	26.70	22.54	18.96	1.370	59.39	46.94
1.140	27.66	23.31	19.61	1.375	60.30	47.47
1.145	28.61	24.08	20.26	1.380	61.27	48.00
1.150	29.57	24.84	20.91	1.385	62.24	48.53
1.155	30.55	25.60	21.55	1.390	63.23	49.06
1.160	31.52	26.36	22.19	1.395	64.25	49.59
1.165	32.49	27.12	22.83	1.400	65.30	50.11
1.170	33.46	27.88	23.47	1.405	66.40	50.63
1.175	34.42	28.63	24.12	1.410	67.50	51.15
1.180	35.39	29.38	24.76	1.415	68.63	51.66
1.185	36.31	30.13	25.40	1.420	69.80	52.15
1.190	37.23	30.88	26.04	1.425	70.98	52.63
1.195	38.16	31.62	26.68	1.430	72.17	53.11
1.200	39.11	32.36	27.32	1.435	73.39	53.59
1.205		33.09	27.95	1.440	74.68	54.07
1.210		33.82	28.58	1.445	75.98	54.55
1.215		34.55	29.21	1.450	77.28	55.03
1.220		35.28	29.84	1.455	78.60	55.50
1.225		36.03	30.48	1.460	79.98	55.97
1.230		36.78	31.11	1.465	81.42	56.43

* From Treadwell and Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons, Inc., by permission.

TABLE VI. SPECIFIC GRAVITY OF STRONG ACIDS AT $\frac{15°}{4°}$ IN VACUO—(*Continued*)

Specific gravity at $\frac{15°}{4°}$ (*vacuo*)	*Per cent by weight*		*Specific gravity at* $\frac{15°}{4°}$ (*vacuo*)	*Per cent by weight*	*Specific gravity at* $\frac{15°}{4°}$ (*vacuo*)	*Per cent by weight*
	HNO_3	H_2SO_4		HS_2O_4		H_2SO_4
1.470	82.90	56.90	1.610	69.56	1.750	81.56
1.475	84.45	57.37	1.615	70.00	1.755	82.00
1.480	86.05	57.83	1 620	70.42	1.760	82.44
1 485	87 70	58.28	1.625	70.85	1.765	83.01
1.490	89.90	58.74	1.630	71.27	1.770	83.51
1 495	91.60	59.22	1.635	71.70	1.775	84.02
1.500	94.09	59.70	1.640	72.12	1.780	84.50
1.505	96.39	60.18	1.645	72.55	1.785	85.10
1.510	98.10	60.65	1.650	72.96	1.790	85.70
1.515	99.07	61.12	1.655	73.40	1.795	86.30
1.520	99.67	61.59	1.660	73.81	1 800	86.92
1.525		62.06	1.665	74.24	1.805	87.60
1.530		62.53	1.670	74 66	1 810	88 30
1.535		63.00	1.675	75.08	1.815	89 16
1.540		63.43	1.680	75.50	1.820	90 05
1.545		63.85	1.685	75.94	1.825	91.00
1.550		64.26	1.690	76.38	1 830	92.10
1.555		64.67	1 695	76.76	1 835	93.56
1.560		65.20	1.700	77.17	1.840	95 60
1.565		65.65	1.705	77.60	1 8405	95.95
1.570		66.09	1.710	78.04	1 8410	96.38
1.575		66.53	1.715	78.48	1.8415	97.35
1.580		66.95	1.720	78.92	1.8410	98 20
1.585		67.40	1 725	79.36	1.8405	98.52
1 590		67.83	1.730	79.80	1.8400	98.72
1.595		68.26	1 735	80.24	1.8395	98.77
1.600		68.70	1.740	80.68	1 8390	99.12
1 605		69 13	1.745	81.12	1.8385	99.31

TABLE VII. THE COMMON LOGARITHMS OF THE NATURAL NUMBERS*

No.	0	1	2	3	4	5	6	7	8	9
100	00 000	00 043	00 087	00 130	00 173	00 217	00 260	00 303	00 346	00 389
101	00 432	00 475	00 518	00 561	00 604	00 647	00 689	00 732	00 775	00 817
102	00 860	00 903	00 945	00 988	01 030	01 072	01 115	01 157	01 199	01 242
103	01 284	01 326	01 368	01 410	01 452	01 494	01 536	01 578	01 620	01 662
104	01 703	01 745	01 787	01 828	01 870	01 912	01 953	01 995	02 036	02 078
105	02 119	02 160	02 202	02 243	02 284	02 325	02 366	02 407	02 449	02 490
106	02 531	02 572	02 612	02 653	02 694	02 735	02 776	02 816	02 857	02 898
107	02 938	02 979	03 019	03 060	03 100	03 141	03 181	03 222	03 262	03 302
108	03 342	03 383	03 423	03 463	03 503	03 543	03 583	03 623	03 663	03 703
109	03 743	03 782	03 822	03 862	03 902	03 941	03 981	04 021	04 060	04 100
110	04 139	04 179	04 218	04 258	04 297	04 336	04 376	04 415	04 454	04 493
111	04 532	04 571	04 610	04 650	04 689	04 727	04 766	04 805	04 844	04 883
112	04 922	04 961	04 999	05 038	05 077	05 115	05 154	05 192	05 231	05 269
113	05 308	05 346	05 385	05 423	05 461	05 500	05 538	05 576	05 614	05 652
114	05 690	05 729	05 767	05 805	05 843	05 881	05 918	05 956	05 994	06 032
115	06 070	06 108	06 145	06 183	06 221	06 258	06 296	06 333	06 371	06 408
116	06 446	06 483	06 521	06 558	06 595	06 633	06 670	06 707	06 744	06 781
117	06 819	06 856	06 893	06 930	06 967	07 004	07 041	07 078	07 115	07 151
118	07 188	07 225	07 262	07 298	07 335	07 372	07 408	07 445	07 482	07 518
119	07 555	07 591	07 628	07 664	07 700	07 737	07 773	07 809	07 846	07 882
120	07 918	07 954	07 990	08 027	08 063	08 099	08 135	08 171	08 207	08 243
121	08 279	08 314	08 350	08 386	08 422	08 458	08 493	08 529	08 565	08 600
122	08 636	08 672	08 707	08 743	08 778	08 814	08 849	08 884	08 920	08 955
123	08 991	09 026	09 061	09 096	09 132	09 167	09 202	09 237	09 272	09 307
124	09 342	09 377	09 412	09 447	09 482	09 517	09 552	09 587	09 621	09 656
125	09 691	09 726	09 760	09 795	09 830	09 864	09 899	09 934	09 968	10 003
126	10 037	10 072	10 106	10 140	10 175	10 209	10 243	10 278	10 312	10 346
127	10 380	10 415	10 449	10 483	10 517	10 551	10 585	10 619	10 653	10 687
128	10 721	10 755	10 789	10 823	10 857	10 890	10 924	10 958	10 992	11 025
129	11 059	11 093	11 126	11 160	11 193	11 227	11 261	11 294	11 327	11 361
130	11 394	11 428	11 461	11 494	11 528	11 561	11 594	11 628	11 661	11 694
131	11 727	11 760	11 793	11 826	11 860	11 893	11 926	11 959	11 992	12 024
132	12 057	12 090	12 123	12 156	12 189	12 222	12 254	12 287	12 320	12 352
133	12 385	12 418	12 450	12 483	12 516	12 548	12 581	12 613	12 646	12 678
134	12 710	12 743	12 775	12 808	12 840	12 872	12 905	12 937	12 969	13 001
135	13 033	13 066	13 098	13 130	13 162	13 194	13 226	13 258	13 290	13 322
136	13 354	13 386	13 418	13 450	13 481	13 513	13 545	13 577	13 609	13 640
137	13 672	13 704	13 735	13 767	13 799	13 830	13 862	13 893	13 925	13 956
138	13 988	14 019	14 051	14 082	14 114	14 145	14 176	14 208	14 239	14 270
139	14 301	14 333	14 364	14 395	14 426	14 457	14 489	14 520	14 551	14 582
140	14 613	14 644	14 675	14 706	14 737	14 768	14 799	14 829	14 860	14 891
141	14 922	14 953	14 983	15 014	15 045	15 076	15 106	15 137	15 168	15 198
142	15 229	15 259	15 290	15 320	15 351	15 381	15 412	15 442	15 473	15 503
143	15 534	15 564	15 594	15 625	15 655	15 685	15 715	15 746	15 776	15 806
144	15 836	15 866	15 897	15 927	15 957	15 987	16 017	16 047	16 077	16 107
145	16 137	16 167	16 197	16 227	16 256	16 286	16 316	16 346	16 376	16 406
146	16 435	16 465	16 495	16 524	16 554	16 584	16 613	16 643	16 673	16 702
147	16 732	16 761	16 791	16 820	16 850	16 879	16 909	16 938	16 967	16 997
148	17 026	17 056	17 085	17 114	17 143	17 173	17 202	17 231	17 260	17 289
149	17 319	17 348	17 377	17 406	17 435	17 464	17 493	17 522	17 551	17 580
150	17 609	17 638	17 667	17 696	17 725	17 754	17 782	17 811	17 840	17 869

* Courtesy, Keasey, Kline, and McIlhatten: *Engineering Mathematics*, The Blakiston Company.

No.	0	1	2	3	4	5	6	7	8	9
150	17 609	17 638	17 667	17 696	17 725	17 754	17 782	17 811	17 840	17 869
151	17 898	17 926	17 955	17 984	18 013	18 041	18 070	18 099	18 127	18 156
152	18 184	18 213	18 241	18 270	18 298	18 327	18 355	18 384	18 412	18 441
153	18 469	18 498	18 526	18 554	18 583	18 611	18 639	18 667	18 696	18 724
154	18 752	18 780	18 808	18 837	18 865	18 893	18 921	18 949	18 977	19 005
155	19 033	19 061	19 089	19 117	19 145	19 173	19 201	19 229	19 257	19 285
156	19 312	19 340	19 368	19 396	19 424	19 451	19 479	19 507	19 535	19 562
157	19 590	19 618	19 645	19 673	19 700	19 728	19 756	19 783	19 811	19 838
158	19 866	19 893	19 921	19 948	19 976	20 003	20 030	20 058	20 085	20 112
159	20 140	20 167	20 194	20 222	20 249	20 276	20 303	20 330	20 358	20 385
160	20 412	20 439	20 466	20 493	20 520	20 548	20 575	20 602	20 629	20 656
161	20 683	20 710	20 737	20 763	20 790	20 817	20 844	20 871	20 898	20 925
162	20 952	20 978	21 005	21 032	21 059	21 085	21 112	21 139	21 165	21 192
163	21 219	21 245	21 272	21 299	21 325	21 352	21 378	21 405	21 431	21 458
164	21 484	21 511	21 537	21 564	21 590	21 617	21 643	21 669	21 696	21 722
165	21 748	21 775	21 801	21 827	21 854	21 880	21 906	21 932	21 958	21 985
166	22 011	22 037	22 063	22 089	22 115	22 141	22 167	22 194	22 220	22 246
167	22 272	22 298	22 324	22 350	22 376	22 401	22 427	22 453	22 479	22 505
168	22 531	22 557	22 583	22 608	22 634	22 660	22 686	22 712	22 737	22 763
169	22 789	22 814	22 840	22 866	22 891	22 917	22 943	22 968	22 994	23 019
170	23 045	23 070	23 096	23 121	23 147	23 172	23 198	23 223	23 249	23 274
171	23 300	23 325	23 350	23 376	23 401	23 426	23 452	23 477	23 502	23 528
172	23 553	23 578	23 603	23 629	23 654	23 679	23 704	23 729	23 754	23 779
173	23 805	23 830	23 855	23 880	23 905	23 930	23 955	23 980	24 005	24 030
174	24 055	24 080	24 105	24 130	24 155	24 180	24 204	24 229	24 254	24 279
175	24 304	24 329	24 353	24 378	24 403	24 428	24 452	24 477	24 502	24 527
176	24 551	24 576	24 601	24 625	24 650	24 674	24 699	24 724	24 748	24 773
177	24 797	24 822	24 846	24 871	24 895	24 920	24 944	24 969	24 993	25 018
178	25 042	25 066	25 091	25 115	25 139	25 164	25 188	25 212	25 237	25 261
179	25 285	25 310	25 334	25 358	25 382	25 406	25 431	25 455	25 479	25 503
180	25 527	25 551	25 575	25 600	25 624	25 648	25 672	25 696	25 720	25 744
181	25 768	25 792	25 816	25 840	25 864	25 888	25 912	25 935	25 959	25 983
182	26 007	26 031	26 055	26 079	26 102	26 126	26 150	26 174	26 198	26 221
183	26 245	26 269	26 293	26 316	26 340	26 364	26 387	26 411	26 435	26 458
184	26 482	26 505	26 529	26 553	26 576	26 600	26 623	26 647	26 670	26 694
185	26 717	26 741	26 764	26 788	26 811	26 834	26 858	26 881	26 905	26 928
186	26 951	26 975	26 998	27 021	27 045	27 068	27 091	27 114	27 138	27 161
187	27 184	27 207	27 231	27 254	27 277	27 300	27 323	27 346	27 370	27 393
188	27 416	27 439	27 462	27 485	27 508	27 531	27 554	27 577	27 600	27 623
189	27 646	27 669	27 692	27 715	27 738	27 761	27 784	27 807	27 830	27 852
190	27 875	27 898	27 921	27 944	27 967	27 989	28 012	28 035	28 058	28 081
191	28 103	28 126	28 149	28 171	28 194	28 217	28 240	28 262	28 285	28 307
192	28 330	28 353	28 375	28 398	28 421	28 443	28 466	28 488	28 511	28 533
193	28 556	28 578	28 601	28 623	28 646	28 668	28 691	28 713	28 735	28 758
194	28 780	28 803	28 825	28 847	28 870	28 892	28 914	28 937	28 959	28 981
195	29 003	29 026	29 048	29 070	29 092	29 115	29 137	29 159	29 181	29 203
196	29 226	29 248	29 270	29 292	29 314	29 336	29 358	29 380	29 403	29 425
197	29 447	29 469	29 491	29 513	29 535	29 557	29 579	29 601	29 623	29 645
198	29 667	29 688	29 710	29 732	29 754	29 776	29 798	29 820	29 842	29 863
199	29 885	29 907	29 929	29 951	29 973	29 994	30 016	30 038	30 060	30 081
200	30 103	30 125	30 146	30 168	30 190	30 211	30 233	30 255	30 276	30 298

No.	0	1	2	3	4	5	6	7	8	9
200	30 103	30 125	30 146	30 168	30 190	30 211	30 233	30 255	30 276	30 298
201	30 320	30 341	30 363	30 384	30 406	30 428	30 449	30 471	30 492	30 514
202	30 535	30 557	30 578	30 600	30 621	30 643	30 664	30 685	30 707	30 728
203	30 750	30 771	30 792	30 814	30 835	30 856	30 878	30 899	30 920	30 942
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206	31 387	31 408	31 429	31 450	31 471	31 492	31 513	31 534	31 555	31 576
207	31 597	31 618	31 639	31 660	31 681	31 702	31 723	31 744	31 765	31 785
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209	32 015	32 035	32 056	32 077	32 098	32 118	32 139	32 160	32 181	32 201
210	32 222	32 243	32 263	32 284	32 305	32 325	32 346	32 366	32 387	32 408
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230	36 173	36 192	36 211	36 229	36 248	36 267	36 286	36 305	36 324	36 342
231	36 361	36 380	36 399	36 418	36 436	36 455	36 474	36 493	36 511	36 530
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237	37 475	37 493	37 511	37 530	37 548	37 566	37 585	37 603	37 621	37 639
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247	39 270	39 287	39 305	39 322	39 340	39 358	39 375	39 393	39 410	39 428
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249	39 620	39 637	39 655	39 672	39 690	39 707	39 724	39 742	39 759	39 777
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252	40 140	40 157	40 175	40 192	40 209	40 226	40 243	40 261	40 278	40 295
253	40 312	40 329	40 346	40 364	40 381	40 398	40 415	40 432	40 449	40 466
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258	41 162	41 179	41 196	41 212	41 229	41 246	41 263	41 280	41 296	41 313
259	41 330	41 347	41 363	41 380	41 397	41 414	41 430	41 447	41 464	41 481
260	41 497	41 514	41 531	41 547	41 564	41 581	41 597	41 614	41 631	41 647
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265	42 325	42 341	42 357	42 374	42 390	42 406	42 423	42 439	42 455	42 472
266	42 488	42 504	42 521	42 537	42 553	42 570	42 586	42 602	42 619	42 635
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271	43 297	43 313	43 329	43 345	43 361	43 377	43 393	43 409	43 425	43 441
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277	44 248	44 264	44 279	44 295	44 311	44 326	44 342	44 358	44 373	44 389
278	44 404	44 420	44 436	44 451	44 467	44 483	44 498	44 514	44 529	44 545
279	44 560	44 576	44 592	44 607	44 623	44 638	44 654	44 669	44 685	44 700
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289	46 090	46 105	46 120	46 135	46 150	46 165	46 180	46 195	46 210	46 225
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292	46 538	46 553	46 568	46 583	46 598	46 613	46 627	46 642	46 657	46 672
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305	48 430	48 444	48 458	48 473	48 487	48 501	48 515	48 530	48 544	48 558
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371	56 937	56 949	56 961	56 972	56 984	56 996	57 008	57 019	57 031	57 043
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373	57 171	57 183	57 194	57 206	57 217	57 229	57 241	57 252	57 264	57 276
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393	59 439	59 450	59 461	59 472	59 483	59 494	59 506	59 517	59 528	59 539
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410	61 278	61 289	61 300	61 310	61 321	61 331	61 342	61 352	61 363	61 374
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417	62 014	62 024	62 034	62 045	62 055	62 066	62 076	62 086	62 097	62 107
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421	62 428	62 439	62 449	62 459	62 469	62 480	62 490	62 500	62 511	62 521
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423	62 634	62 644	62 655	62 665	62 675	62 685	62 696	62 706	62 716	62 726
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438	64 147	64 157	64 167	64 177	64 187	64 197	64 207	64 217	64 227	64 237
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449	65 225	65 234	65 244	65 254	65 263	65 273	65 283	65 292	65 302	65 312
450	65 321	65 331	65 341	65 350	65 360	65 369	65 379	65 389	65 398	65 408

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456	65 896	65 906	65 916	65 925	65 935	65 944	65 954	65 963	65 973	65 982
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459	66 181	66 191	66 200	66 210	66 219	66 229	66 238	66 247	66 257	66 266
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462	66 464	66 474	66 483	66 492	66 502	66 511	66 521	66 530	66 539	66 549
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488	68 842	68 851	68 860	68 869	68 878	68 886	68 895	68 904	68 913	68 922
489	68 931	68 940	68 949	68 958	68 966	68 975	68 984	68 993	69 002	69 011
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571	75 664	75 671	75 679	75 686	75 694	75 702	75 709	75 717	75 724	75 732
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575	75 967	75 974	75 982	75 989	75 997	76 005	76 012	76 020	76 027	76 035
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617	79 029	79 036	79 043	79 050	79 057	79 064	79 071	79 078	79 085	79 092
618	79 099	79 106	79 113	79 120	79 127	79 134	79 141	79 148	79 155	79 162
619	79 169	79 176	79 183	79 190	79 197	79 204	79 211	79 218	79 225	79 232
620	79 239	79 246	79 253	79 260	79 267	79 274	79 281	79 288	79 295	79 302
621	79 309	79 316	79 323	79 330	79 337	79 344	79 351	79 358	79 365	79 372
622	79 379	79 386	79 393	79 400	79 407	79 414	79 421	79 428	79 435	79 442
623	79 449	79 456	79 463	79 470	79 477	79 484	79 491	79 498	79 505	79 511
624	79 518	79 525	79 532	79 539	79 546	79 553	79 560	79 567	79 574	79 581
625	79 588	79 595	79 602	79 609	79 616	79 623	79 630	79 637	79 644	79 650
626	79 657	79 664	79 671	79 678	79 685	79 692	79 699	79 706	79 713	79 720
627	79 727	79 734	79 741	79 748	79 754	79 761	79 768	79 775	79 782	79 789
628	79 796	79 803	79 810	79 817	79 824	79 831	79 837	79 844	79 851	79 858
629	79 865	79 872	79 879	79 886	79 893	79 900	79 906	79 913	79 920	79 927
630	79 934	79 941	79 948	79 955	79 962	79 969	79 975	79 982	79 989	79 996
631	80 003	80 010	80 017	80 024	80 030	80 037	80 044	80 051	80 058	80 065
632	80 072	80 079	80 085	80 092	80 099	80 106	80 113	80 120	80 127	80 134
633	80 140	80 147	80 154	80 161	80 168	80 175	80 182	80 188	80 195	80 202
634	80 209	80 216	80 223	80 229	80 236	80 243	80 250	80 257	80 264	80 271
635	80 277	80 284	80 291	80 298	80 305	80 312	80 318	80 325	80 332	80 339
636	80 346	80 353	80 359	80 366	80 373	80 380	80 387	80 393	80 400	80 407
637	80 414	80 421	80 428	80 434	80 441	80 448	80 455	80 462	80 468	80 475
638	80 482	80 489	80 496	80 502	80 509	80 516	80 523	80 530	80 536	80 543
639	80 550	80 557	80 564	80 570	80 577	80 584	80 591	80 598	80 604	80 611
640	80 618	80 625	80 632	80 638	80 645	80 652	80 659	80 665	80 672	80 679
641	80 686	80 693	80 699	80 706	80 713	80 720	80 726	80 733	80 740	80 747
642	80 754	80 760	80 767	80 774	80 781	80 787	80 794	80 801	80 808	80 814
643	80 821	80 828	80 835	80 841	80 848	80 855	80 862	80 868	80 875	80 882
644	80 889	80 895	80 902	80 909	80 916	80 922	80 929	80 936	80 943	80 949
645	80 956	80 963	80 969	80 976	80 983	80 990	80 996	81 003	81 010	81 017
646	81 023	81 030	81 037	81 043	81 050	81 057	81 064	81 070	81 077	81 084
647	81 090	81 097	81 104	81 111	81 117	81 124	81 131	81 137	81 144	81 151
648	81 158	81 164	81 171	81 178	81 184	81 191	81 198	81 204	81 211	81 218
649	81 224	81 231	81 238	81 245	81 251	81 258	81 265	81 271	81 278	81 285
650	81 291	81 298	81 305	81 311	81 318	81 325	81 331	81 338	81 345	81 351

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650	81 291	81 298	81 305	81 311	81 318	81 325	81 331	81 338	81 345	81 351
651	81 358	81 365	81 371	81 378	81 385	81 391	81 398	81 405	81 411	81 418
652	81 425	81 431	81 438	81 445	81 451	81 458	81 465	81 471	81 478	81 485
653	81 491	81 498	81 505	81 511	81 518	81 525	81 531	81 538	81 544	81 551
654	81 558	81 564	81 571	81 578	81 584	81 591	81 598	81 604	81 611	81 617
655	81 624	81 631	81 637	81 644	81 651	81 657	81 664	81 671	81 677	81 684
656	81 690	81 697	81 704	81 710	81 717	81 723	81 730	81 737	81 743	81 750
657	81 757	81 763	81 770	81 776	81 783	81 790	81 796	81 803	81 809	81 816
658	81 823	81 829	81 836	81 842	81 849	81 856	81 862	81 869	81 875	81 882
659	81 889	81 895	81 902	81 908	81 915	81 921	81 928	81 935	81 941	81 948
660	81 954	81 961	81 968	81 974	81 981	81 987	81 994	82 000	82 007	82 014
661	82 020	82 027	82 033	82 040	82 046	82 053	82 060	82 066	82 073	82 079
662	82 086	82 092	82 099	82 105	82 112	82 119	82 125	82 132	82 138	82 145
663	82 151	82 158	82 164	82 171	82 178	82 184	82 191	82 197	82 204	82 210
664	82 217	82 223	82 230	82 236	82 243	82 249	82 256	82 263	82 269	82 276
665	82 282	82 289	82 295	82 302	82 308	82 315	82 321	82 328	82 334	82 341
666	82 347	82 354	82 360	82 367	82 373	82 380	82 387	82 393	82 400	82 406
667	82 413	82 419	82 426	82 432	82 439	82 445	82 452	82 458	82 465	82 471
668	82 478	82 484	82 491	82 497	82 504	82 510	82 517	82 523	82 530	82 536
669	82 543	82 549	82 556	82 562	82 569	82 575	82 582	82 588	82 595	82 601
670	82 607	82 614	82 620	82 627	82 633	82 640	82 646	82 653	82 659	82 666
671	82 672	82 679	82 685	82 692	82 698	82 705	82 711	82 718	82 724	82 730
672	82 737	82 743	82 750	82 756	82 763	82 769	82 776	82 782	82 789	82 795
673	82 802	82 808	82 814	82 821	82 827	82 834	82 840	82 847	82 853	82 860
674	82 866	82 872	82 879	82 885	82 892	82 898	82 905	82 911	82 918	82 924
675	82 930	82 937	82 943	82 950	82 956	82 963	82 969	82 975	82 982	82 988
676	82 995	83 001	83 008	83 014	83 020	83 027	83 033	83 040	83 046	83 052
677	83 059	83 065	83 072	83 078	83 085	83 091	83 097	83 104	83 110	83 117
678	83 123	83 129	83 136	83 142	83 149	83 155	83 161	83 168	83 174	83 181
679	83 187	83 193	83 200	83 206	83 213	83 219	83 225	83 232	83 238	83 245
680	83 251	83 257	83 264	83 270	83 276	83 283	83 289	83 296	83 302	83 308
681	83 315	83 321	83 327	83 334	83 340	83 347	83 353	83 359	83 366	83 372
682	83 378	83 385	83 391	83 398	83 404	83 410	83 417	83 423	83 429	83 436
683	83 442	83 448	83 455	83 461	83 467	83 474	83 480	83 487	83 493	83 499
684	83 506	83 512	83 518	83 525	83 531	83 537	83 544	83 550	83 556	83 563
685	83 569	83 575	83 582	83 588	83 594	83 601	83 607	83 613	83 620	83 626
686	83 632	83 639	83 645	83 651	83 658	83 664	83 670	83 677	83 683	83 689
687	83 696	83 702	83 708	83 715	83 721	83 727	83 734	83 740	83 746	83 753
688	83 759	83 765	83 771	83 778	83 784	83 790	83 797	83 803	83 809	83 816
689	83 822	83 828	83 835	83 841	83 847	83 853	83 860	83 866	83 872	83 879
690	83 885	83 891	83 897	83 904	83 910	83 916	83 923	83 929	83 935	83 942
691	83 948	83 954	83 960	83 967	83 973	83 979	83 985	83 992	83 998	84 004
692	84 011	84 017	84 023	84 029	84 036	84 042	84 048	84 055	84 061	84 067
693	84 073	84 080	84 086	84 092	84 098	84 105	84 111	84 117	84 123	84 130
694	84 136	84 142	84 148	84 155	84 161	84 167	84 173	84 180	84 186	84 192
695	84 198	84 205	84 211	84 217	84 223	84 230	84 236	84 242	84 248	84 255
696	84 261	84 267	84 273	84 280	84 286	84 292	84 298	84 305	84 311	84 317
697	84 323	84 330	84 336	84 342	84 348	84 354	84 361	84 367	84 373	84 379
698	84 386	84 392	84 398	84 404	84 410	84 417	84 423	84 429	84 435	84 442
699	84 448	84 454	84 460	84 466	84 473	84 479	84 485	84 491	84 497	84 504
700	84 510	84 516	84 522	84 528	84 535	84 541	84 547	84 553	84 559	84 566

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700	84 510	84 516	84 522	84 528	84 535	84 541	84 547	84 553	84 559	84 566
701	84 572	84 578	84 584	84 590	84 597	84 603	84 609	84 615	84 621	84 628
702	84 634	84 640	84 646	84 652	84 658	84 665	84 671	84 677	84 633	84 689
703	84 696	84 702	84 708	84 714	84 720	84 726	84 733	84 739	84 745	84 751
704	84 757	84 763	84 770	84 776	84 782	84 788	84 794	84 800	84 807	84 813
705	84 819	84 825	84 831	84 837	84 844	84 850	84 856	84 862	84 868	84 874
706	84 880	84 887	84 893	84 899	84 905	84 911	84 917	84 924	84 930	84 936
707	84 942	84 948	84 954	84 960	84 967	84 973	84 979	84 985	84 991	84 997
708	85 003	85 009	85 016	85 022	85 028	85 034	85 040	85 046	85 052	85 058
709	85 065	85 071	85 077	85 083	85 089	85 095	85 101	85 107	85 114	85 120
710	85 126	85 132	85 138	85 144	85 150	85 156	85 163	85 169	85 175	85 181
711	85 187	85 193	85 199	85 205	85 211	85 217	85 224	85 230	85 236	85 242
712	85 248	85 254	85 260	85 266	85 272	85 278	85 285	85 291	85 297	85 303
713	85 309	85 315	85 321	85 327	85 333	85 339	85 345	85 352	85 358	85 364
714	85 370	85 376	85 382	85 388	85 394	85 400	85 406	85 412	85 418	85 425
715	85 431	85 437	85 443	85 449	85 455	85 461	85 467	85 473	85 479	85 485
716	85 491	85 497	85 503	85 509	85 516	85 522	85 528	85 534	85 540	85 546
717	85 552	85 558	85 564	85 570	85 576	85 582	85 588	85 594	85 600	85 606
718	85 612	85 618	85 625	85 631	85 637	85 643	85 649	85 655	85 661	85 667
719	85 673	85 679	85 685	85 691	85 697	85 703	85 709	85 715	85 721	85 727
720	85 733	85 739	85 745	85 751	85 757	85 763	85 769	85 775	85 781	85 788
721	85 794	85 800	85 806	85 812	85 818	85 824	85 830	85 836	85 842	85 848
722	85 854	85 860	85 866	85 872	85 878	85 884	85 890	85 896	85 902	85 908
723	85 914	85 920	85 926	85 932	85 938	85 944	85 950	85 956	85 962	85 968
724	85 974	85 980	85 986	85 992	85 998	86 004	86 010	86 016	86 022	86 028
725	86 034	86 040	86 046	86 052	86 058	86 064	86 070	86 076	86 082	86 088
726	86 094	86 100	86 106	86 112	86 118	86 124	86 130	86 136	86 141	86 147
727	86 153	86 159	86 165	86 171	86 177	86 183	86 189	86 195	86 201	86 207
728	86 213	86 219	86 225	86 231	86 237	86 243	86 249	86 255	86 261	86 267
729	86 273	86 279	86 285	86 291	86 297	86 303	86 308	86 314	86 320	86 326
730	86 332	86 338	86 344	86 350	86 356	86 362	86 368	86 374	86 380	86 386
731	86 392	86 398	86 404	86 410	86 415	86 421	86 427	86 433	86 439	86 445
732	86 451	86 457	86 463	86 469	86 475	86 481	86 487	86 493	86 499	86 504
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734	86 570	86 576	86 581	86 587	86 593	86 599	86 605	86 611	86 617	86 623
735	86 629	86 635	86 641	86 646	86 652	86 658	86 664	86 670	86 676	86 682
736	86 688	86 694	86 700	86 705	86 711	86 717	86 723	86 729	86 735	86 741
737	86 747	86 753	86 759	86 764	86 770	86 776	86 782	86 788	86 794	86 800
738	86 806	86 812	86 817	86 823	86 829	86 835	86 841	86 847	86 853	85 859
739	86 864	86 870	86 876	86 882	86 888	86 894	86 900	86 906	86 911	86 917
740	86 923	86 929	86 935	86 941	86 947	86 953	86 958	86 964	86 970	86 976
741	86 982	86 988	86 994	86 999	87 005	87 011	87 017	87 023	87 029	87 035
742	87 010	87 046	87 052	87 058	87 064	87 070	87 075	87 081	87 087	87 093
743	87 099	87 105	87 111	87 116	87 122	87 128	87 134	87 140	87 146	87 151
744	87 157	87 163	87 169	87 175	87 181	87 186	87 192	87 198	87 204	87 210
745	87 216	87 221	87 227	87 233	87 239	87 245	87 251	87 256	87 262	87 268
746	87 274	87 280	87 286	87 291	87 297	87 303	87 309	87 315	87 320	87 326
747	87 332	87 338	87 344	87 349	87 355	87 361	87 367	87 373	87 379	87 384
748	87 390	87 396	87 402	87 408	87 413	87 419	87 425	87 431	87 437	87 442
749	87 448	87 454	87 460	87 466	87 471	87 477	87 483	87 489	87 495	87 500
750	87 506	87 512	87 518	87 523	87 529	87 535	87 541	87 547	87 552	87 558

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750	87 506	87 512	87 518	87 523	87 529	87 535	87 541	87 547	87 552	87 558
751	87 564	87 570	87 576	87 581	87 587	87 593	87 599	87 604	87 610	87 616
752	87 622	87 628	87 633	87 639	87 645	87 651	87 656	87 662	87 668	87 674
753	87 679	87 685	87 691	87 697	87 703	87 708	87 714	87 720	87 726	87 731
754	87 737	87 743	87 749	87 754	87 760	87 766	87 772	87 777	87 783	87 789
755	87 795	87 800	87 806	87 812	87 818	87 823	87 829	87 835	87 841	87 846
756	87 852	87 858	87 864	87 869	87 875	87 881	87 887	87 892	87 898	87 904
757	87 910	87 915	87 921	87 927	87 933	87 938	87 944	87 950	87 955	87 961
758	87 967	87 973	87 978	87 984	87 990	87 996	88 001	88 007	88 013	88 018
759	88 024	88 030	88 036	88 041	88 047	88 053	88 058	88 064	88 070	88 076
760	88 081	88 087	88 093	88 098	88 104	88 110	88 116	88 121	88 127	88 133
761	88 138	88 144	88 150	88 156	88 161	88 167	88 173	88 178	88 184	88 190
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765	88 366	88 372	88 377	88 383	88 389	88 395	88 400	88 406	88 412	88 417
766	88 423	88 429	88 434	88 440	88 446	88 451	88 457	88 463	88 468	88 474
767	88 480	88 485	88 491	88 497	88 502	88 508	88 513	88 519	88 525	88 530
768	88 536	88 542	88 547	88 553	88 559	88 564	88 570	88 576	88 581	88 587
769	88 593	88 598	88 604	88 610	88 615	88 621	88 627	88 632	88 638	88 643
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771	88 705	88 711	88 717	88 722	88 728	88 734	88 739	88 745	88 750	88 756
772	88 762	88 767	88 773	88 779	88 784	88 790	88 795	88 801	88 807	88 812
773	88 818	88 824	88 829	88 835	88 840	88 846	88 852	88 857	88 863	88 868
774	88 874	88 880	88 885	88 891	88 897	88 902	88 908	88 913	88 919	88 925
775	88 930	88 936	88 941	88 947	88 953	88 958	88 964	88 969	88 975	88 981
776	88 986	88 992	88 997	89 003	89 009	89 014	89 020	89 025	89 031	89 037
777	89 042	89 048	89 053	89 059	89 064	89 070	89 076	89 081	89 087	89 092
778	89 098	89 104	89 109	89 115	89 120	89 126	89 131	89 137	89 143	89 148
779	89 154	89 159	89 165	89 170	89 176	89 182	89 187	89 193	89 198	89 204
780	89 209	89 215	89 221	89 226	89 232	89 237	89 243	89 248	89 254	89 260
781	89 265	89 271	89 276	89 282	89 287	89 293	89 298	89 304	89 310	89 315
782	89 321	89 326	89 332	89 337	89 343	89 348	89 354	89 360	89 365	89 371
783	89 376	89 382	89 387	89 393	89 398	89 404	89 409	89 415	89 421	89 426
784	89 432	89 437	89 443	89 448	89 454	89 459	89 465	89 470	89 476	89 481
785	89 487	89 492	89 498	89 504	89 509	89 515	89 520	89 526	89 531	89 537
786	89 542	89 548	89 553	89 559	89 564	89 570	89 575	89 581	89 586	89 592
787	89 597	89 603	89 609	89 614	89 620	89 625	89 631	89 636	89 642	89 647
788	89 653	89 658	89 664	89 669	89 675	89 680	89 686	89 691	89 697	89 702
789	89 708	89 713	89 719	89 724	89 730	89 735	89 741	89 746	89 752	89 757
790	89 763	89 768	89 774	89 779	89 785	89 790	89 796	89 801	89 807	89 812
791	89 818	89 823	89 829	89 834	89 840	89 845	89 851	89 856	89 862	89 867
792	89 873	89 878	89 883	89 889	89 894	89 900	89 905	89 911	89 916	89 922
793	89 927	89 933	89 938	89 944	89 949	89 955	89 960	89 966	89 971	89 977
794	89 982	89 988	89 993	89 998	90 004	90 009	90 015	90 020	90 026	90 031
795	90 037	90 042	90 048	90 053	90 059	90 064	90 069	90 075	90 080	90 086
796	90 091	90 097	90 102	90 108	90 113	90 119	90 124	90 129	90 135	90 140
797	90 146	90 151	90 157	90 162	90 168	90 173	90 179	90 184	90 189	90 195
798	90 200	90 206	90 211	90 217	90 222	90 227	90 233	90 238	90 244	90 249
799	90 255	90 260	90 266	90 271	90 276	90 282	90 287	90 293	90 298	90 304
800	90 309	90 314	90 320	90 325	90 331	90 336	90 342	90 347	90 352	90 358

No.	0	1	2	3	4	5	6	7	8	9
800	90 309	90 314	90 320	90 325	90 331	90 336	90 342	90 347	90 352	90 358
801	90 363	90 369	90 374	90 380	90 385	90 390	90 396	90 401	90 407	90 412
802	90 417	90 423	90 428	90 434	90 439	90 445	90 450	90 455	90 461	90 466
803	90 472	90 477	90 482	90 488	90 493	90 499	90 504	90 509	90 515	90 520
804	90 526	90 531	90 536	90 542	90 547	90 553	90 558	90 563	90 569	90 574
805	90 580	90 585	90 590	90 596	90 601	90 607	90 612	90 617	90 623	90 628
806	90 634	90 639	90 644	90 650	90 655	90 660	90 666	90 671	90 677	90 682
807	90 687	90 693	90 698	90 703	90 709	90 714	90 720	90 725	90 730	90 736
808	90 741	90 747	90 752	90 757	90 763	90 768	90 773	90 779	90 784	90 789
809	90 795	90 800	90 806	90 811	90 816	90 822	90 827	90 832	90 838	90 843
810	90 849	90 854	90 859	90 865	90 870	90 875	90 881	90 886	90 891	90 897
811	90 902	90 907	90 913	90 918	90 924	90 929	90 934	90 940	90 945	90 950
812	90 956	90 961	90 966	90 972	90 977	90 982	90 988	90 993	90 998	91 004
813	91 009	91 014	91 020	91 025	91 030	91 036	91 041	91 046	91 052	91 057
814	91 062	91 068	91 073	91 078	91 084	91 089	91 094	91 100	91 105	91 110
815	91 116	91 121	91 126	91 132	91 137	91 142	91 148	91 153	91 158	91 164
816	91 169	91 174	91 180	91 185	91 190	91 196	91 201	91 206	91 212	91 217
817	91 222	91 228	91 233	91 238	91 243	91 249	91 254	91 259	91 265	91 270
818	91 275	91 281	91 286	91 291	91 297	91 302	91 307	91 312	91 318	91 323
819	91 328	91 334	91 339	91 344	91 350	91 355	91 360	91 365	91 371	91 376
820	91 381	91 387	91 392	91 397	91 403	91 408	91 413	91 418	91 424	91 429
821	91 434	91 440	91 445	91 450	91 455	91 461	91 466	91 471	91 477	91 482
822	91 487	91 492	91 498	91 503	91 508	91 514	91 519	91 524	91 529	91 535
823	91 540	91 545	91 551	91 556	91 561	91 566	91 572	91 577	91 582	91 587
824	91 593	91 598	91 603	91 609	91 614	91 619	91 624	91 630	91 635	91 640
825	91 645	91 651	91 656	91 661	91 666	91 672	91 677	91 682	91 687	91 693
826	91 698	91 703	91 709	91 714	91 719	91 724	91 730	91 735	91 740	91 745
827	91 751	91 756	91 761	91 766	91 772	91 777	91 782	91 787	91 793	91 798
828	91 803	91 808	91 814	91 819	91 824	91 829	91 834	91 840	91 845	91 850
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842	92 531	92 536	92 542	92 547	92 552	92 557	92 562	92 567	92 572	92 578
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AUTHOR INDEX

Allen, A. H., 329
Allen, W. S., 254
Altieri, J., 329
Arenson, S. B., 329
Ayers, G. H., 317

Baudisch, O., 278
Baxter, G. P., 187
Becker, Christian, Co., 43
Been, J., 242
Beer, A., 317
Bishop, H. B., 254
Blade, E., 57
Blakiston Co., 15, 27, 40, 41, 44
Blasdale, W. C., 242, 329
Booth, H. S., 17, 329
Bradstreet, R. B., 143
Braithwaite, L., 244
Bray, W. C., 213
Bright, H. A., 189, 330
Briscoe, H. T., 105
Britton, H. M. P., 53
Brönsted, J. N., 86
Brown, J., 278
Brunck, O., 275
Buford, M. G., 313

Caley, E. R., 313
Clark, W. M., 101, 105, 329
Crumpler, T. B., 329

Damerell, V. R., 329
Debye, P., 105
Demorest, D. J., 313, 330
Diehl, H., 329
Dole, M., 297, 329

Eastman Kodak Co., 132
Edmonds, S. M., 194

Fales, H. A., 191, 239, 244, 278, 329
Fisher, H. J., 329
Fisher Scientific Co., 42
Foot, H. W., 216
Foulk, C. W., 135
Fowler, R. H., 189
Freundlich, H., 241
Furman, H. N., 199, 293, 329

Getz, C. A., 199
Gibb, M., 320
Goodrich, B. F., Co., 131
Griffin, C. W., 14

Haenisch, E. L., 329
Hahn, F. L., 213, 277
Hall, N. F., 86
Hall, W. T., 335, 336
Hamilton, L. T., 329, 330
Hammett, L. P., 194
Heston, B. O., 145
Hillebrand, W. F., 17, 263, 277, 278, 329
Hoffman, J. I., 259, 330
Hollingsworth, M., 135
Hückel, E., 105
Hume, D. N., 193
Hurley, F. H., 57

Jacobs, M. B., 330
Johnson, W. C., 86

Kanning, E. W., 329
Kar, H. A., 278
Kassner, E. E., 212
Kassner, J. L., 212
Keasey, M. A., 338
Kenny, F., 191, 244, 278, 329
Kline, G. A., 338
Knowles, H. B., 277
Kolthoff, I. M., 31, 104, 181, 184, 226, 242, 243, 252, 277, 329, 330
Kuhn, O., 46
Kunz, A. H., 199

Laitinen, H. A., 330
Lambert, J. H., 317
Launer, H. F., 189
Leach, A. E., 330
Leblanc, M., 306
Lehrman, L., 242
Lewis, G. N., 229
Lin, I., 53
Lingane, J. J., 194, 196
Lord, N. W., 313, 330
Low, A. H., 330
Lowry, T. M., 86

Lundell, G. E. F., 259, 263, 277, 278, 329, 330

Machlett, E., and Son, 146
Manes, M., 242
McBride, R. S., 189
McIlhatten, D. A., 338
McIntire, L., 17
Meeker, E. W., 147
Meites, L., 194
Mellan, I., 330
Mellor, J. W., 267
Miller, H. E., 213
Moore, H. C., 254
Muller, R. H., 320
Murphy, W. J., 330
Muskovitz, B., 242

Naiman, B., 198, 206, 329
Nernst, W., 167
Neuss, J. D., 198, 329
Nichols, M. S., 206

Oesper, R. E., 143, 199, 329
Ostwald, W., 101

Parr, S. W., 330
Pedersen, K. J., 244
Pierce, W. C., 329
Platow, A. M., 206
Popoff, S., 213
Prodinger, W., 275

Randall, M., 229
Razim, W. W., 28
Richards, T. W., 57
Rieman, W., 198, 243, 329

Sand, H. J. S., 330
Sandell, E. B., 31, 181, 184, 226, 243, 252, 277, 329
Sargent, E. H., Co., 43
Sarver, L. A., 330
Schneider, F., 243
Schoder, W. P., 330
Scott, W. W., 207, 313, 329
Semon, W. L., 57
Simpson, R. B., 141
Simpson, S. G., 329, 330
Smith, E. F., 306
Smith, G. F., 199
Smith, G. F., Chemical Co., 136, 145, 200
Snell, C. T., 330
Snell, F. D., 330
Sörensen, S. L. P., 88
Soule, B. A., 131
Southern, J. A., 275, 277
Steinmetz, M. H., 207
Stenger, V. A., 84, 104, 184, 329
Stone, H. W., 193
Sutton, F. A., 330

Talbot, H. P., 329
Taylor, H. S., 13
Thompson, W. S., 239
Thornton, W. M., 57
Treadwell, F. P., 335, 336

Vance, J. E., 216
Viewig, K., 277
von Saaf, M., 14

Wagner, E. C., 147
Walden, G. H., 194
Wallace, J. H., 199
Weinig, A. J., 330
Whitman, J. L., 213
Willard, H. H., 199, 202, 317, 329
Winkler, L. W., 147
Winton, A. L., 330
Wood, S. R., 145
Woodman, A. G., 330

Yoe, J. H., 317, 329, 330
Yost, D. M., 189
Young, P., 199, 202

Zanetti, J. E., 187

SUBJECT INDEX

Page numbers set in **boldface** refer to notes following a procedure. The letter "n" following a page number refers to a footnote on that page.

A

Absorbents, for carbon dioxide, 271
  for water, 15, 271
Absorption in weighing, 63
Accidental errors, 26
Accuracy and precision, 24
Acetic acid, density and composition of, 84
  determination of, 138
  ionization constant of, 331
  titration curve of, 113
Acid potassium phthalate, 136
Acidimetry and alkalimetry, 130
  exercises in, 138
  theory of, 86, 130
Acidity, Brönsted concept of, 86
  effect of, in electrolysis, 306
  of acetic acid, 138
  of oxalic acid, 138
  of vinegar, 138
  pH scale of, 88
Acids (*see also* Acidimetry and alkalimetry)
  density and composition of, 84, 336
  determination of, 138
    potentiometric, 300
  ionization constants of, 331
  standard for, 132 (*see also* Criteria for standards)
  standardization of, 132
  strength of concentrated, 84
  titration curves of, 108, 113, 120, 123
  weak, ionization of, 89
Activity, 105, 228
  and standard state, 173
  coefficient, 105, 228
  of unity, for hydrogen ion, 168
Adsorption, 241
  by precipitates, 241
  indicators, 288
  isotherm, 241
  of moisture in weighing, 274
Air, buoyancy correction for, in weighing, 55
Air—(*Continued*)
  density of, 56
Alcohol, use of, in drying precipitates, **250**
Alkalies (*see also* Acidimetry and alkalimetry)
  determination of, 140, 141
  standardization of, 136
  standards for, 136 (*see also* Criteria for standards)
Alloys, brass, 312
  coinage, 311
  iron-nickel, 276
Alphabenzoinoxime, 278
Alphanitrosobetanapthol, 278
Aluminum, determination of, 277
  oxide, in combined oxides, 266
Amalgamated zinc, 193
Ammonia, density of, 335
Ammonium molybdate reagent, 257
Ammonium salts, destruction of, 270
Analysis, colorimetric, 317
  gravimetric, theory of, 221
    experimental, 248
  indirect, 155
  preliminary qualitative, 1
  spectrographic, 1
  volumetric, 130, 187
Analytical balance, 39
Analytical weights, 42
  calibration of, 57
  tolerances of, 45
Anhydrone, 271
Anode, sign of, 172
Antimony, determination of, 208, 209
Apparatus, glass, test for cleanliness of, 18n
Arsenious oxide, as standard for ceric sulfate, 200
  as standard for iodine, 206
  as standard for permanganate, 189
Asbestos mat for Gooch crucible, 10
Ascarite as absorbent for carbon dioxide, 271
Atomic weights, table of, *inside back cover*

Available chlorine, determination of, 216
Average deviation, 27

B

Balance, analytical, 39
  air-damped, 42
  chainomatic, 41
  construction of, 39
  equilibrium point of, 46
  inequality of length of arms of, 51, 51
  keyboard, 41
  magnetic-damped, 42
  rest point of, 46
  rules for use of, 45
  sensitivity of, 48, 50
  theory of, 48
Balanced watch glasses, 63
Balancing oxidation-reduction equations, 157
Ball mill for grinding, 6
Barium sulfate, properties of, 251
Bases, carbonate-free, preparation of, 131
  ionization constants of, 331
  standardization of, 136, 137
  weak, titration curve of, 116
Beer's law, 317
Bicarbonate, pH of solutions of, 96
  titration curve of, 123
Bi-iodate, potassium, as standard, 213
Blanks in analyses, 32
Bleaching powder, determination of chlorine in, 216
Borda's method of weighing, 55
Boric acid, titration of, 139
  titration curve of, 113
  use of, in Kjeldahl analysis, 147
Brass, analysis of, 312
Bromate, potassium, and iodate, comparison of, as oxidants, 210
  as standard, 213
Bromcresol green indicator, 148
Bromide, determination of, gravimetric, 248
  volumetric, by Fajans method, 291
    by Mohr method, 284
    by Volhard method, 286
Bromphenol blue indicator, 101
Brönsted theory of acids and bases, 86
Buffers, 97
  most effective, 98
  preparation of, 98
  resistance of, to change in pH, 99
Buret, 20
  calibration of, 71
  cleanliness of, test for, 18n
  parallax in reading of, 21

C

Calcium, determination of, in limestone, 267
    volumetric, 196, 198
Calcium chloride as desiccant, 271
Calcium oxalate precipitate, treatment of, in analysis for calcium, 268
Calcium oxide, as weighing form for calcium, 268
  hygroscopicity of, 63
Calcium sulfate as weighing form for calcium, 268
Calculations, acid-base titration curves, 104
  electrode potentials and electromotive force, 175, 295
  oxidation-reduction, 159
  precipitation titrations, 282
  solubility product, 222
  volumetric analysis, 78–84
Calibration, of volumetric apparatus, 65
    buret, 71
    flask, 66
    pipet, 70
    table for, 68
  of weights, 57
    absolute, 59
    relative, 57
Calomel electrode, 168, 183, 293, 296
Carbon dioxide, determination of, 270
    apparatus for, 272
Carbon dioxide-free water, preparation of, 126n
  use of, 125
Carbonate, titration of, 122
    in presence of alkali or bicarbonate, 124, 141
  titration curve of, 123
Carbonate-free base, preparation of, 131
Cathode, sign of, 172
Cells, electromotive force of, 169
    calomel-hydrogen, 295
    calomel-quinhydrone, 298
    calomel-silver, 300
    cerium-hydrogen, 175
    cerium-iron, 175
    cerium-tin, 177
    copper-chlorine, 303
    copper-hydrogen, 170
    copper-zinc, 170, 306
    iron-hydrogen, 175
    silver-hydrogen, 168
Ceric ammonium sulfate, 199, 200
  preparation of standard solution of, 200
  standardization of, with arsenious oxide, 200

Ceric ammonium sulfate—(*Continued*)
standardization of—(*Continued*)
with iron wire, 201
titration with, 180
Ceric sulfate as oxidant, 199
Cerium, oxidation potential, variability of, 199n
Chainomatic balance, 41
Chloride, determination of, by Fajans method, 290
by Mohr method, 283
by Volhard method, 286
gravimetric, 248
potentiometric, 302
Chloride-free water, test for, **250**
Chlorine, available, in bleaching powder, determination of, 216
Choice of proper indicator, 104
Chromite, 219
Chromophore, 102
Citrate, alkaline, preparation of, 258
Citric acid, ionization constants of, 331
Cleanliness, 4
test for, in glassware, 18n
Colloids, 239
colligative properties of, 239
Color change, in acid-base indicators, 101
in oxidation-reduction indicators, 184
Colorimeter, 319
use of, 322
Colorimetric apparatus, 319–321
Colorimetric determination, of hydrogen ion, 321
of manganese, 322
Colorimetry, 317
comparison solutions in, 321
theory of, 317–318
Combined oxides, determination of, in limestone, 266
Common ion effect, 224, 226, 227
Comparison solutions, in colorimetry, 321
Completeness of electrolytic separations, 305
Completeness of reaction, calculation of, 179
Complex ions and solubility, 230
Complex ions in electroanalysis, 307
Concentration, methods of expressing, 74
of laboratory reagents, 84
of standard solutions, 130
relation of, to electromotive force, 176
Coning of sample, 6
Constant boiling hydrochloric acid, 135
preparation of, 135
pressure-composition table for, 135
Constant errors, 25
Constant weight, attainment of, 15, 17
Constants, equilibrium, 331, 332
Contamination, from grinding, 6n
of precipitates, 238
of reagents, 5
Control runs, 33
Copper, determination of, electrolytic, 308
in brass, 314
in copper-nickel alloys, 311
iodometric, 215
Coprecipitation, 238
minimization of, 245
Corrections for analytical weights, 61
table of, 62
Counterpoise, in determination of carbon dioxide, **274**
in weighing, 55
Criteria for standards, 78
Crucibles, filtering, 10
for fusions, 8
Gooch, 10
Crushing of sample for analysis, 6
Crystals, occlusion in, 243
size of, 9
structure of, 221
vapor pressure of hydrates of, 16
Cubic centimeter, definition of, 65
Cupferron, 278
Current density, 305
Cyanide, determination of, by Liebig method, 285

D

Damped balances, 42, 43
Data, recording of, 4, 133, 134
Decantation, washing by, 10
Decomposition voltage, 304
Dehydration of silica, 265
Density, of acids, 84, 336
of air, 56
of ammonia, 84, 335
of water, 68
Desiccants, 15, 271
Desiccator, 15
Determinate errors, 25
Deviation, average, of arithmetic mean, 27
of single measurement, 27
Dextrin in prevention of coagulation, **290**
Diameter of molecules and suspensoid particles, 239
Dichlorofluorescein adsorption indicator, 290
Dichromate as oxidant, 201
Digestion, in Kjeldahl analysis, 144
of precipitates, 8

Dilution to definite normality, 83, 84
Dimethylglyoxime, 275
  in determination of nickel in steel, 276
Diphenylamine indicator, 185
Diphenylamine sulfonic acid indicator, 185
Diphenylbenzidine indicator, 185
Disk, perforated, for Gooch crucible, 10
Dissociation, of weak electrolytes, 89–91
  constants, 331
Distillation of ammonia by Kjeldahl analysis, 145
Distribution constant, 13
Double indicator titrations, 124
Double layer, electrical, 166
    between colloid particles and indicator, 288
Double precipitation, 245
Drierite, 271
Drying, glassware, 67n
  precipitates, 14

E

Efficiency of desiccants, 15
Electrical double layer, 166
Electrification, effect in weighing, 63
Electroanalysis, apparatus for, 308
  effect of acidity in, 306
  theory of, 303
Electrode, 167
  calomel, 168, 293, 296
  glass, 297
  hydrogen, 168, 295, 296
  indicator, 293
  quinhydrone, 298
  reference, 293
  sign of, 170, 172
  silver, 168
Electrode potential (*see also* Oxidation-reduction, theory of)
  and equilibrium concentration, 165
  and oxidation-reduction reactions, 174
  and standard state, 173
  asymmetry, 297
  at stoichiometric point, 180
  change of, during titration, 179
  measurement of, 168
  molar, 167
    table of, 171
  single, 167
Electrodeposition, 307
  completeness of, 306
Electrodes, for electroanalysis, 308
  indicator, 293
  reference, 293
Electrolysis, analysis by, 307
Electrolytic determination, of copper, 308, 311
  of lead, 313
  of nickel, 311
Electrometric titrations, 293
Electromotive force, relation of, to concentration, 176
Electron affinity, 170, 172
Electrophotometer, 320
Electrostatic attraction, 166
End point of titration, 74
Eosin as adsorption indicator, 290
Equations, oxidation-reduction, balancing of, 157
Equilibrium concentration, 165
Equilibrium constants, calculation of, 178
  tables of, 331, 332
Equilibrium point in weighing, 46
Equipment, 4
Equivalence point in titrations, 74
Equivalent weight, 76
  of oxidants and reductants, 153
Erasures, 4
Error curve, 27
Errors, 25
  accidental, 26
  constant, 25
  determinate, 25
  effect of, on final result, 36
  indeterminate, 26
  instrumental, 25
  in weighing, 62
  methodic, 25
  minimization and correction of, 32
  personal, 25
  probable, 28
  standard, 28
Eschka method for determination of sulfur, 255
Ether, drying precipitates with, 250
Evaporation, 8
External indicators, 202, 203, 291
Extraction, process of, 13

F

Fajans method for determination of halides, 290
Faraday's law, 303
Ferric iron, reduction of, by Jones reductor, 192
    by stannous chloride, 191
Ferric oxide, hydrous, properties of, 260
Ferroin indicator, 184
Figures, significant, 33
Filter paper, ashless, selection of, 9
Filtration of precipitate, 9

Flasks, volumetric, 18
calibration of, 66
Fluorescein as adsorption indicator, 289
Flux in fusions, 7
Fractional precipitation, 233, 281
regulation of, by controlled pH, 234
Freundlich adsorption equation, 241
Fusions, 7

G

Gas absorption train, 272
Gauss method of weighing, 54
Gels, 240
General operations, 4
Glassware, cleanliness of, test for, 18n
Glycerol, use of, in titrating boric acid, 139
Gooch crucible, 10
Gram equivalent weight, 2, 3, 76
Gram milliequivalent weight, 2, 3, 76
Graphs, for sensitivity of balance, 51
for titration, of acids, 108, 113, 120, 123
of bases, 116
of sodium carbonate, 123
showing common ion effect, 226, 227
Gravimetric analysis, experimental, 248
fundamental principles, 221
Gravimetric standardization of hydrochloric acid, 132n
Grinding, excessive, 6n

H

Hehner cylinders, 320
Hydrochloric acid, constant boiling, 135
density of solutions of, 84, 336
preparation of standard solution of, 130
standardization of, 133, 135
Hydrofluoric acid for volatilization of silica, 266
Hydrogen electrode, 168, 295, 296
Hydrogen ion concentration, and solubility, 232
in buffer solutions, 97
in hydrolyzed salt solutions, 91–97
in mixtures of weak acids and salts, 97
in mixtures of weak bases and salts, 98
in strong acids, 89
in titrations, 104–128
in water, 88
in weak acids, 89
in weak bases, 91
methods of expressing, 87
value at neutrality, 88
Hydrogen peroxide, acetanilide in, 199
Hydrogen peroxide—(*Continued*)
determination of, by iodometric method, 217
by permanganate method, 198
Hydrogen sulfide, determination of, by iodimetric method, 207
ionization constants of, 331
reduction with, 191
Hydrolysis constant, 92, 93
Hydrolysis of salt solutions, 91–97
Hydronium ion, 86
Hydrophilic colloids, 240
Hydrophobic colloids, 239
Hydrosols, 239
Hydrous oxides, 260
Hydroxyl ion concentration, in water, 88
in weak base, 91
8-Hydroxyquinoline, 277
use of, in determination of aluminum, 277
Hygroscopicity in weighing, 63

I

Ignition of precipitates, 15
Indicator electrode, 293
Indicators, acid-base, 100
choice of, 104
external, 202, 203, 291
mixed, 104
modified methyl orange, 132
phenolphthalein, 102
range of, 100, 103
table of, 101
theory of, 101
transition pH of, 100, 101
oxidation-reduction, 183
diphenylamine, 185
diphenylamine sulfonic acid, 185
diphenylbenzidine, 185
ferroin, 184
preparation of, 200
nitro-ferroin, 185
orthophenanthroline-ferrous ion, 185
preparation of, 200
precipitation titration, chromate, 281, 283
dichlorofluorescein, 290
eosin, 290
ferric thiocyanate ion, 286
fluorescein, 289
silver iodide, 285
spot test, 202, 203, 291
starch, 205
preparation of, 205
Indirect analysis, 155, 156

International atomic weights, *inside back cover*
In vacuo weight, 55
  of water, 69
Invert sugar, use of, in titration of boric acid, 139
Iodate, and bromate, comparison of, as oxidants of iodide, 210
  as oxidant, 210
Iodide, determination of, Fajans method of, 291
    gravimetric, 218
    Volhard method of, 286
  oxidation of, by air, 213
  separation of, from chloride, 234
Iodimetry, 204, 206
  reactions of, 204
Iodine, preparation of standard solution of, 206
  processes of analysis, 204
  solution, stability of, 206
  standardization of, 207
Iodometry, 204, 210
  reactions of, 204
Ionic strength, 229
Ionization constants, of acids, 331
  of bases, 331
Iron, as primary standard, 190, 201, 202
  determination of, gravimetric, 260
    in brass, 314
    in coinage alloys or monel metal, 311
    volumetric method, by ceric sulfate, 201
      by dichromate, 203
      by permanganate, 190
  reduction of ferric to ferrous, 191, 192
Iron ores, composition of, 190
  determination of iron in, 190
Iron oxide, properties of, 260

J

Jaw crusher, 6
Jones reductor, 192
  air in, 194, 195
  zero blank of, 194

K

Kjeldahl method for nitrogen, 143, 148

L

Laboratory notebook, 4
Laboratory work, efficiency during, 5
Lambert's law, 317
Law of mass action, 222
Lead, determination of, as dioxide, electrolytic, 313
    gravimetric, 274
Lead oxides, analysis of, 195
Lead sulfate as weighing form for lead, 274
Liebig method for determination of cyanide, 284, 285
Limestone, analysis of, 262
  composition of, 263
Limits of error in analytical weights, 45
Liter, definition of, 65
Logarithms, table of, 338
Loss on ignition, of limestone, 263

M

Magnesia mixture, preparation of, 257
Magnesium, determination of, in limestone, 269
Magnesium ammonium phosphate, coprecipitation with, 256
  ignition of, 256
Magnesium oxalate, coprecipitation of, by calcium oxalate, 267
Magnesium perchlorate as desiccant, 271
Manganese, determination of, colorimetric, 322
    in pyrolusite, volumetric, 195
Manitol, use of, in titration of boric acid, 139
Mass, definition of, 39
Mass action, law of, 222
Measurements, number of, 30
  reliability of mean results of, 30
Meniscus, 21
Mercuric chloride reagent, 191, 192
Methyl orange, 101, 125, 134
Methyl red, 101
Milliequivalent, 2
Milliliter, definition of, 65
  difference between, and cubic centimeter, 65
Mixed indicators, 104
Modified methyl orange, 132
Mohr method for determination of halide, 283
  theory of, 281
Mohr pipet, 18
Moisture, determination of, in limestone, 263
Molar hydrogen electrode, 168
Molar solutions, 75
Molecular diameter, 239
Molecular weights, table of, 333
Molybdate as reagent, 257
Mortar, agate, for grinding, 6

N

Nernst equation, 167
Nessler tubes, 321
Neutralization, 86
  definition of, 88
Neutralization curves, 104–125
Nickel, determination of, electrolytic, 311
    gravimetric, with dimethylglyoxime, 276
Nickel crucibles, 8
Nitrate, determination of, 148
Nitric acid, density of solutions of, 84, 336
Nitrite, determination of, 148
Nitrogen, determination of, 143, 148
Nitrosophenylhydroxylamine, 278
Normal solutions, 75, 76
Normality, calculation of, 80
    for solutions of oxidants and reductants, 156
  definite, dilution of solutions to, 83, 84
Nucleation and crystal growth, 240

O

Occlusion, 243
Operations, general, 4
Organic matter, destruction of, 144, 190
Organic precipitants, 274
Orthophenanthroline-ferrous ion indicator, 185
Osmium tetroxide as catalyst, 200
Osmotic pressure, 166
Overvoltage, 304
Oxalic acid, determination of acidity of, 138
Oxidation, definition of, 152
Oxidation number, 153
Oxidation potentials, table of, 171
Oxidation-reduction, 152
  calculations, 159
  completeness of reaction, 179
  effect of concentration in, 176
  equations, balancing of, 157
  equivalent weights in, 153
  experimental, 187, 299
  indicators, 183
  stoichiometric relations in, 152
  theory of, 164
Oxidizing agents, table of, 154
Oxidizing fluxes, 8
Oxine, 277

P

Paper, filter, selection of, 9
Parallax, 21
Particle size, 239
Peptization, 11, 240
Percentage basis for expressing concentrations, 74
Perchloric acid, and organic matter, 7n
  as solvent, 7
Periodate as oxidant for manganese, 322
Permanganate processes, 187 (*see also* Potassium permanganate)
Peroxide, hydrogen, determination of, by iodometric method, 217
    by permanganate method, 198
Persulfate as oxidant for manganese, 322
pH, 88
  and neutrality, 88
  and solubility, 232
  in buffer solution, 97
  in hydrolyzed salt solutions, 91–97
  in mixtures of weak acids and salts, 97
  in mixtures of weak bases and salts, 98
  in strong acids, 89
  in titrations, 104–128
  in weak acids, 89
  in weak bases, 91
Phase rule, 16
Phenol red indicator, 101
Phenolphthalein indicator, 101
  structure of, 102
Phosphoric acid, ionization constants of, 331
  titration of, 122
  titration curve of, 123
Phosphorus, determination of, by phosphomolybdate method, 256
    by short method, 259
Phosphorus pentoxide desiccant, 15
Pipet, 18, 19
  calibration of, 70
  cleanliness of, test for, 18n
  Mohr, 18
  use of, 18
Platinum ware, care of, 327
  fusions in, 8
Polarity of cells, 172–174
Policeman, 10
Postprecipitation, 244
  of calcium oxalate, 197
Potassium bi-iodate as primary standard, 213
Potassium biphthalate as primary standard, 136
Potassium bromate, as oxidant of iodide, 210
  as primary standard, 213
Potassium dichromate processes, 201

Potassium dichromate—(*Continued*)
standard solution of, 202
standardization of, with iron wire, 202
Potassium iodate, as oxidant of iodide, 210
as primary standard, 213
Potassium permanganate, advantages of, as oxidant, 187
oxidation potential of, 171
preparation of standard solution of, 188
processes, 187
standardization of, with arsenious oxide, 189
with iron wire, 190
with sodium oxalate, 189
use of, as oxidant, 188
Potassium thiocyanate, preparation of standard solution of, 287
Potential, asymmetry, 297
decomposition, 304
liquid junction, 169
oxidation, table of, 171
single electrode, 167
Potentiometer, 293–295
Potentiometric titrations, 293
oxidation-reduction, 299, 301
precipitation, 300, 302
using glass electrode, 301
using hydrogen electrode, 300
using quinhydrone electrode, 301
Precipitates, adsorptive properties of, 241
drying of, 14
filtration of, 9
ignition of, 14
subdivision of liquid in washing of, 12
transfer of, to funnel, 11
washing of, by decantation, 10
Precipitation, analysis, volumetric, 281
completeness of, 224
fractional, 233, 281
theory of, 221
with organic precipitants, 274
Precision, 24
computation of, 24–25
Preservatives for starch solution, 206n
Preventive solution in determination of iron, 191
Primary standards, criteria of, 78
Probability curve, 27
Probability of deviations, 31
Process of extraction, 13
Proton acceptor, 86
Proton donor, 86
Proximate analysis, 263
Pyrite, determination of sulfur in, 254
Pyrolusite, analysis of, 195

Q

Quadratic equation, approximation in solving, 110n
Qualitative analysis, 1
Quantitative analysis, 1
Quartering of sample, 6
Quinhydrone electrode, 298

R

Ratio of lengths of balance arms, 54
Reagent bottles, 5
Reagents, density and composition of, 84
Records, 4
Reducing agents for ferric ion, 191
Reduction, definition of, 152
of weighings to vacuo, 55
of water, 69
Reference books, 329
Reference electrode, 293
Refractive index, 1
Rejection of a result, 30
Reliability of mean result, 28
Removal of ammonium salts, 270
Reprecipitation, 245
Rest point of balance, 46
Rider, 40
Rubber paint, 131n

S

Salt bridge, 169
Salt effect, 227
Salts, hydrolysis of, 91
solubility of, 224
Sample, change in composition of, by grinding, 6n
crushing of, 6
grab, 6
size of, 6, 37
solution of, 7
tabling of, 6
weighing of, 6
Sensitivity of balance, 48
curve of, 51
determination of, 50
factors influencing, 48
Separations, by electrolysis, 305
by formation of complex ions, 307
Significant figures, 33
in computations, 34
Silica, dehydration of, 265
determination of, 264
purified, determination of, 265
Silicates, decomposition of, 7
Silver, determination of, gravimetric, 248